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NEW FORMIC ACID FUEL CELL ORIENTATIONS
TO REDUCE THE COST OF CELL COMPONENTS

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Engineering

By

John Calvin Holtkamp
B.S., Wright State University, 2006

2009
Wright State University

WRIGHT STATE UNIVERSITY
SCHOOL OF GRADUATE STUDIES

September 18, 2009

I HEREBY RECOMMEND THAT THIS THESIS PREPARED UNDER MY
SUPERVISION BY John Holtkamp ENTITLED New Formic Acid Fuel Cell
Orientations to Reduce the Cost of Cell Components BE ACCEPTED IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of
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ABSTRACT

Holtkamp, John Calvin. M.S., Department of Materials Engineering, Wright State University, 2009. New Formic Acid Fuel Cell Orientation to Reduce the Cost of Cell Components.

Formic acid fuel cells show the potential of outperforming or replacing direct methanol fuel cells. A number of issues need to be overcome in order for fuel cells, specifically formic acid fuel cells, to be seriously considered for use in small electronic devices. One of the largest issues inhibiting the commercial success of fuel cells is the costs of the components. The catalyst and ion-conducting membrane, key components in a fuel cell, are both expensive. With the current amount of costly materials needed to construct a fuel cell, fuel cells will have limited success in becoming mainstream power sources in the near future. The focus of this research is to construct a new formic acid fuel cell orientation which can replace the expensive ion-conducting membrane with a more cost effective component.

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I. INTRODUCTION

The main objective of this project is to design a new formic acid fuel cell configuration that eliminates the need for a high cost, ion-conducting membrane. Currently Nafion, a product of DuPont, is commonly used in PEM (polymer electrolyte membrane) fuel cells. The high cost of this membrane, along with the catalyst, is one of the major factors hindering fuel cells from entering the main stream population as a source for powering handheld electronics.

In order to change the configuration of a formic acid fuel cell, a number of factors needed to be simultaneously developed, modified, and optimized. These factors include the fuel cell housing, anode and cathode catalyst, and the membrane. All three of these factors are addressed in this project. Each of these design choices alone are important and could be optimized beyond what is discussed in this paper. The project scope discussed in this paper did not encompass a complete optimization and further research is needed in this area.

The fuel cell housing was prepared by mixing exfoliated graphite with phenolic resin, and then pressing the mixture. This produces a soft, conductive shell. Testing was preformed to optimize the ratio of graphite to resin to produce the best conductivity.

The catalyst was prepared by a sodium borohydride (NaBH_4) reduction reaction which produced carbon supported palladium (Pd/C). Palladium was

selected, and despite its rarity, the cost is nearly an order of magnitude less than platinumⁱ. Platinum is the common anode and cathode catalyst in hydrogen fuel cells. The procedure for producing carbon supported palladium is used by the University of Illinois, as well as a number of other organizations. The procedure was modified slightly.

The new membrane was selected based on its ability to “wick” the formic acid and remain saturated with it. The formic acid was used as the fuel as well as the ion-conducting medium in the membrane material. By using foam that can be saturated with formic acid, the expensive ion-conducting membrane can be replaced by a relatively inexpensive material.

A new fuel cell configuration was produced following the steps mentioned above. The resulting fuel cell was tested thoroughly and the results were tabulated.

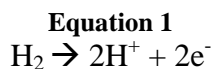
II. BACKGROUND

FUEL CELL BASICS:

A PEM (polymer electrolyte membrane) fuel cell is designed to generate power by supplying hydrogen and oxygen to a cell. For a fuel cell to function, it is necessary for a chemical reaction to occur. In this reaction, an electron separates from an atom, and the atom becomes an ion. The electron will travel through an electrically conductive electrode and out of the fuel cell to provide power. In order for the fuel cell to function, the ion that formed when the electron was extracted from an atom needs to cross an electrolyte. The ion will react on the opposite side of the electrolyte in a reaction that will yield water.

The difference between a PEM fuel cell and other types of fuel cells is that the electrolyte is made of a polymer. The significance of a PEM fuel cell is that it can be used at room temperature (or temperatures near room temperature), while most other fuel cells need to be operated at higher temperatures.

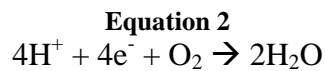
In a PEM fuel cell, the series of reactions that was mentioned above will begin at the anode side of the fuel cell. In the most basic type of PEM fuel cell, hydrogen (H_2) will be supplied to the anode. A catalyst on the anode helps in separating the H_2 into $2H^+$ (two ions) and $2e^-$ (two electrons). Equation 1 shows the reaction equation for the hydrogen being separated.



The electrons will travel through an electrically conductive electrode, out of the fuel cell, into what the fuel cell is being used to power, and back into the cathode side of the fuel cell where the electron will be involved in a reaction to produce water.

The hydrogen ion will cross the polymer electrolyte membrane due to a concentration gradient (dc/dx). This membrane is necessary because the ion can cross it, but the electrons cannot because the membrane is not electrically conductive. A majority of the H_2 molecule at the anode are also blocked from crossing the membrane. The hydrogen ion will cross the membrane from the anode side to the cathode side.

Oxygen is supplied to the cathode side. The catalyst at the cathode initiates a reaction between the oxygen, hydrogen ions, and electrons to form water, as can be seen in Equation 2.



Losses in performance are introduced in each part of the fuel cell (anode, cathode, electrolyte, and connections). These losses can be caused by bad connections and low conductivity of ions (ohmic losses), sluggish reactions (activation losses), and issues with providing enough fuel to the cell (mass transport losses), and other inefficiencies in the system.

A fuel cell's polarization curve, a plot showing the voltage at different currents to discern the performance of a fuel cell, shows the losses mentioned above. Figure 1ⁱⁱ, a hypothetical polarization curve, depicts where the different

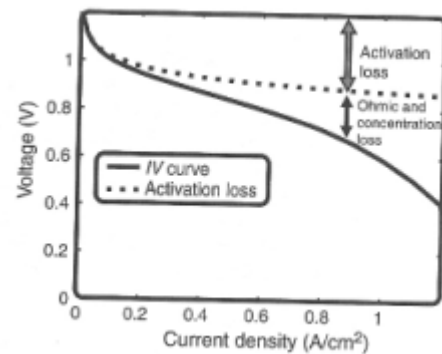


Figure 1: Polarization curve

losses take place.

At low currents (to the far left of the plot in Figure 1), there is a large negative slope, causing the cell voltage to drop significantly with little rise in the current. This is due to activation losses. In the middle portion of the plot the slope evens out but is still negative to a lesser magnitude. In this current range, the losses are mainly ohmic losses. To the far right, at a higher current, the losses mainly consist of mass transport losses.

Ohmic losses are concerned with interconnects and ionic conductivity. These losses involve the electrolyte, the GDL/GDE, and the wires which transfer the electrons from the anode to the cathode outside of the cell. The mass transport losses are due to the inability to supply fuel fast enough at high currents, and due to the undesired pathways taken by a portion of the O_2 , H^+ , and electrons to the cathode. Activation losses concern the reaction kinetics at the cathode and anode, and this directly relates to the catalysts.

A fuel cell commonly functions in the current range where ohmic losses are the main concern, but the activation losses still impact the fuel cell voltage while operating at a given current, even in the ohmic range. As seen in Figure 1, if there are significant activation losses, when the current is high enough to be in the ohmic loss range, the voltage will already be too low. This means that even if the ohmic losses are very low (making the ohmic loss region nearly horizontal), the voltage will still be too low due to the fact that activation losses were so high. The opposite can also be true. If the activation losses are relatively low, the ohmic loss range will have a higher voltage at a given current.

In a fuel cell, the catalyst is commonly applied to a cloth or paper made of carbon. The carbon transfers the electrons to the external circuit while the ions are transferred

through the electrolyte. This is mentioned because abbreviations such as Pt/C may be used. Pd/C signifies that platinum is dispersed on carbon.

THE ION CONDUCTING MEMBRANE

The polymer electrolyte membrane is an ionomer. An ionomer is a co-polymer, with a large part of the polymer consisting of non-ionic repeating units, and a small portion (<15%) consisting of ionic repeating units. The ions transfer through the membrane by hopping through these ionic sites (from ionic site to ionic site). In the case of the PEM fuel cell where hydrogen ions are crossing the electrolyte, there are negatively charged ions in the repeating units. These ions are used as sites that the positively charged hydrogen ion can hop to.

For the electrolyte to be a suitable ion conductor, two important physical properties are the presence of fixed charge sites (as was mentioned in the previous paragraph) and free volume. Free volume is the presence of small pore structures within the polymer which increase the range of small-scale structural vibrations. The motion can allow the physical transfer of ions from site to site through the polymer. Both fixed charge sites and free volume can weaken the polymer, so their presence must be limited.

An example of an ionomer is ethylene methacrylic acid. Though this ionomer is not used in fuel cells, it gives an introduction to ionomers and their formation. Ethylene and methacrylic acid are used to form this ionomer. Figure 2ⁱⁱⁱ shows this combination.

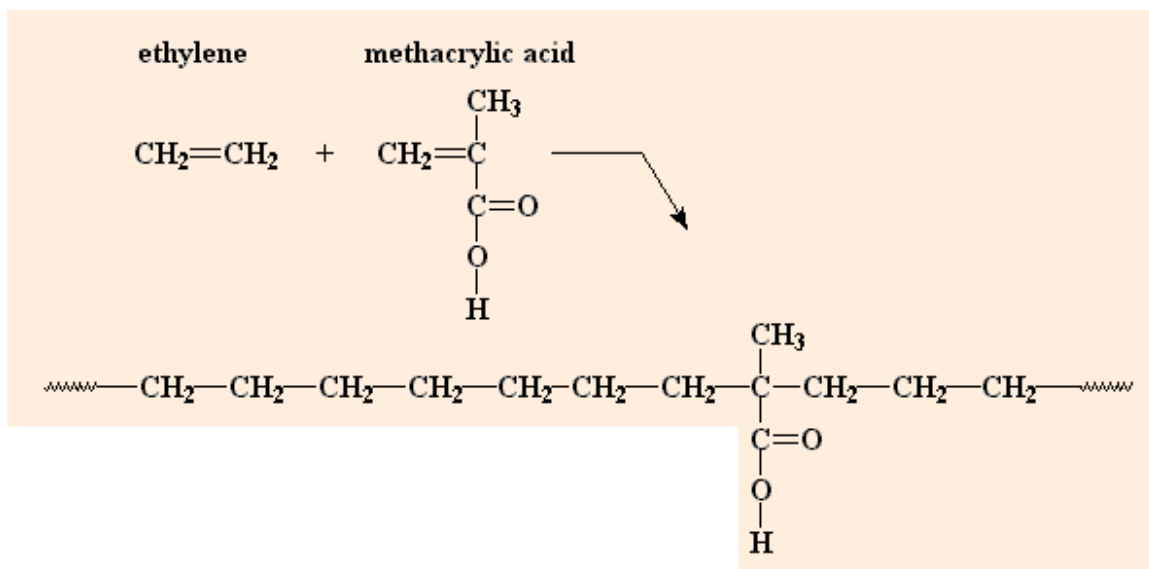


Figure 2: Combination of ethylene and methacrylic acid in order to form an ionomer

If molecules such as NaOH are used to neutralize the acid in the ionomer, the OH^- will break from the Na and attach to the H^+ from the acid to form H_2O . The Na^+ will be attracted to the O^- that is left at the end of the acid after the H^+ has broken off and result in Figure 3ⁱⁱⁱ.

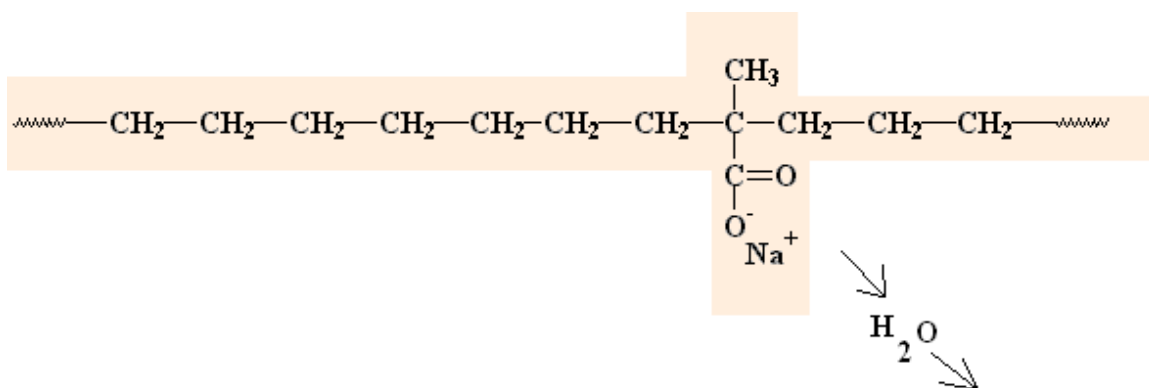


Figure 3: Sodium neutralized ionomer

The ionomer will have a backbone which is non-ionic, but has branches which consist of acid. These branches tend to group together as pictured in Figure 4ⁱⁱⁱ to form

what appears to be cross-linking between the backbones, however, they are not cross-linked. As the material is heated, the clustered groups will break apart because the ionic attraction is not strong enough to hold them together. This property of ionomers makes them have the processability of a thermoplastic, but some properties of a crosslinked polymer at lower temperatures, making them thermoplastic elastomers.

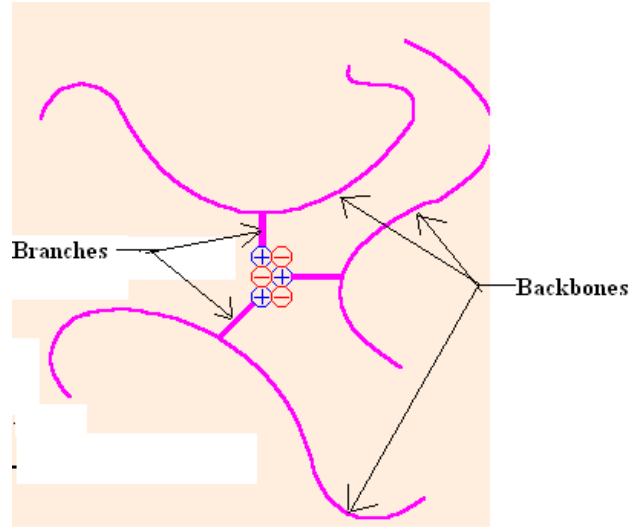


Figure 4: Branches from the polymer backbone cluster together

The clumping of ionic groups in a polymer influences its properties. Some of these properties are the enhancing of tear resistance, glass transition temperature, and ionic conductivity. These property enhancements are believed to be the result of the ionic clumps acting as physical cross links.

Nafion is the primary ionomer which is in PEM fuel cells. There have been many models for Nafion, but it is unknown exactly how the ionic groups clump together in Nafion. A very simple view showing the phase separation between the polar and non-polar regions of Nafion can be found in Figure 5^{iv}. What is shown in this figure are the

hydrophobic (repels hydrogen) Teflon backbones wrapped around the hydrophilic (accepts hydrogen) clusters of ionic groups.

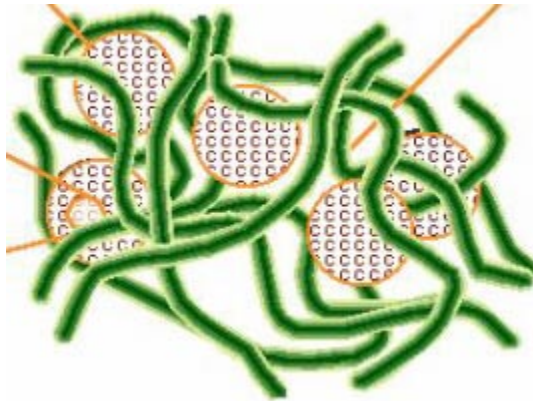


Figure 5: Picture of separation between ionic and non-ionic phases in Nafion. The long strands are the Teflon backbone (non-ionic), and the circular areas are the ionic clusters.

Pictured in Figure 6^{iv} is the Yeager Three Phase Model. As the name suggests, the model is separated into three areas. It has a Teflon (PTFE) backbone, interface regions, and cluster regions where most of the ionic sites come together.

In the region containing the Teflon backbone, water and H^+ ions should not be found because the Teflon is hydrophobic. The interface region contains a relatively high fractional void volume (volume of voids / volume of material). In this region, portions of the side chains as well as some water can be found. In the cluster region, sulfonic acid is found (SO_3^-). Figure 6 is not accurate for cluster region of Nafion used in fuel cells. This is because there are two types of Nafion. One has sodium, which is attached to the SO_3^- (sodium form of Nafion, which is not used in fuel cells), and the other model has hydrogen which is attached to the SO_3^- (acid form of Nafion, which is used in fuel cells). If the Na^+ were removed from Figure 6 and replaced with H^+ , it would show the type of Nafion used in fuel cells. This ionic “cluster” region, created by the SO_3H , attracts water

and creates the sites for the H^+ to jump to and from. This is why this region contains most of the ionic exchange sites as well as the absorbed water.

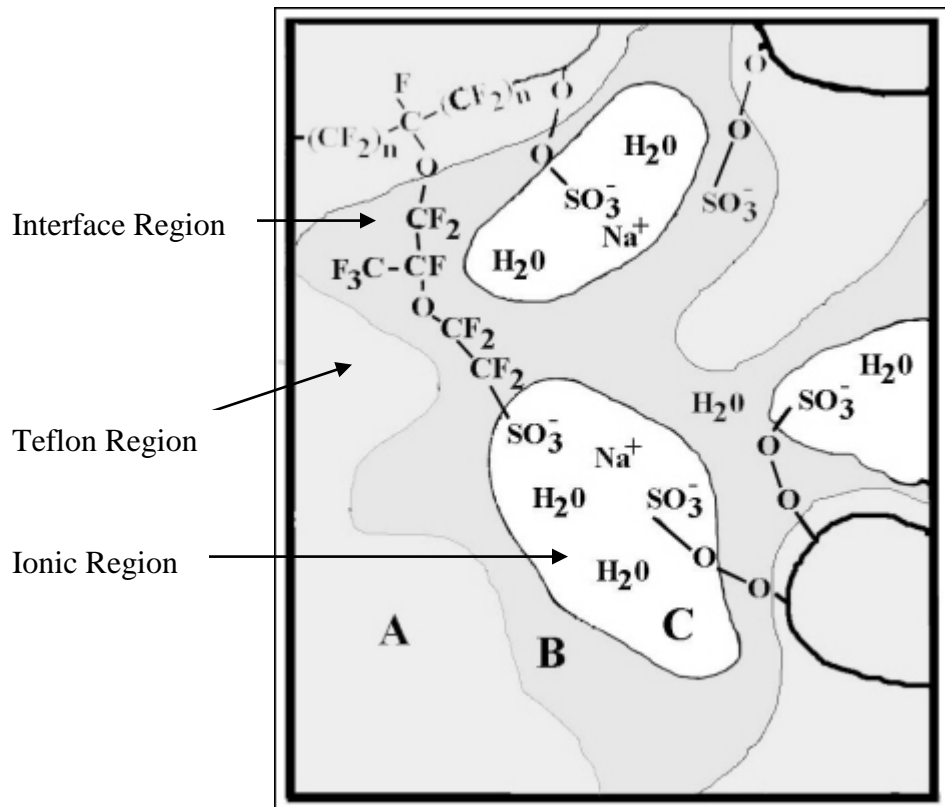


Figure 6: Yeager model for Nafion consisting of three regions.

There are two mechanisms that the hydrogen ions are believed to use to travel through Nafion. The first is by a hopping mechanism, and the second is a vehicle mechanism.

With the hopping mechanism, the H^+ ions that were a product of the reaction on the anode side of the fuel cell are forced through the PEM by a concentration gradient. This gradient is caused by the fact that there are hydrogen ions on the anode side, and none on the cathode side (the hydrogen on the cathode side is reacting to form water that is released from the fuel cell). It is believed that the H^+ ions will hop to a SO_3H site and

attach to the SO_3^- . This will force the H that was previously bonded to the SO_3^- to be broken away as an H^+ ion and move farther through the PEM to react with another SO_3H . After a series of these H^+ ions attaching to SO_3H and sending new H^+ ions further through the PEM, an H^+ ion will eventually reach the cathode side to react with the oxygen, electron, and another H^+ ion to form water. Figure 7^v shows the hopping mechanism as it occurs in ice.

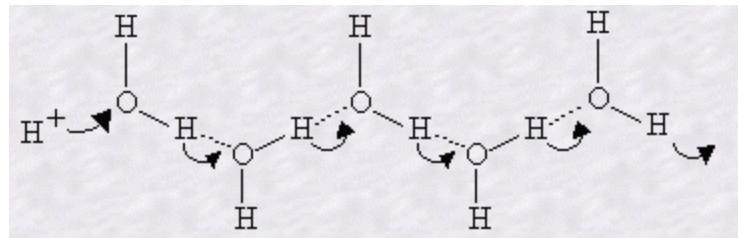


Figure 7: Ionic hopping mechanism in ice.

A vehicle mechanism involves ions being pulled along by a free species, known as the vehicle. In the case of hydrogen ions being pulled through Nafion, water is the vehicle species. This is why it is important for Nafion to be fully hydrated, which causes it to swell.

The Nafion is hydrated by humidifying the hydrogen and oxygen that is fed to the anode and cathode of the fuel cell. Water is believed to enter pores (voids) whose walls contain SO_3H . The water will take the H^+ from the SO_3^- and form H_3O^+ (hydronium). If there is significant hydration, the hydronium can transport the H^+ in the aqueous phase through the PEM.

Due to the high cost of Nafion, a significant research field for fuel cells is in developing a new PEM that works similar to or better than Nafion. A short list of some polymers that could be used to derive PEM structures are polysulfones, polyetherketones PEEK, poly(4-phenocycbenzoyl-1,4-phenylene), and PPBP. The use of any of these

polymers is dependent of it having a charge group introduced to it. This can be done by sulfonation.

The sulfonation of a PEEK and a PPBP monomer is pictured in Figure 8^{vi}. As Figure 8 depicts, H_2SO_4 is added to the monomer, and a hydrogen and oxygen ion from H_2SO_4 react with a hydrogen atom on a benzene ring to form water (H_2O), and the SO_3H that is left bonds where the hydrogen atom was bonded to the benzene ring.

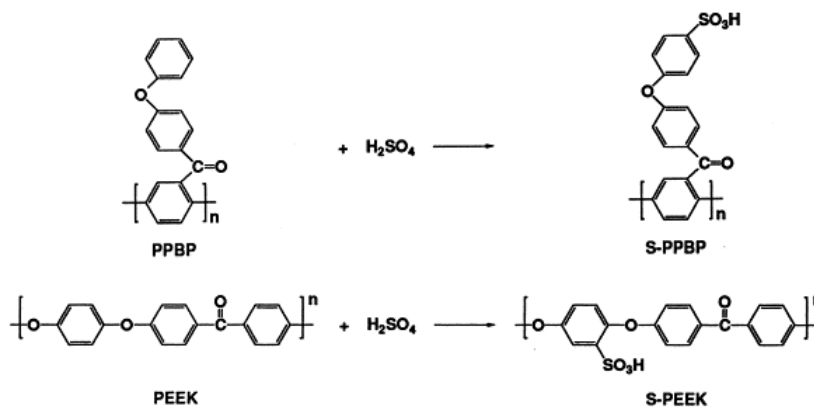


Figure 8: Sulfonation of PPBP and PEEK to form negatively charged sites for ionic conduction.

The sulfonated PEEK and PPBP reached ionic conductivities as high as 10^{-5} S/cm and 10^{-2} S/cm respectively at 100% relative humidity^{vi}. Nafion has an ionic conductivity around 7.8×10^{-2} S/cm at 100% relative humidity. This shows that sulfonated PPBP is comparable to Nafion performance, but PEEK is not.

DIFFUSION THROUGH THE ELECTROLYTE

In a basic case, diffusion through polymers takes place through free volume (vacancies) or interstitials (between molecular chains). Though diffusion can occur due to

other causes (temperature gradients, chemical potential gradients, etc...), the cause most commonly considered is diffusion due to a concentration gradient. This is the case that is expressed by Fick's laws, which will be considered later.

Diffusion can be affected by multiple factors which are accounted for in the diffusion coefficient. These factors can include crystallinity, fillers used, temperature, penetrant size, penetrant polarity, and the polymer's molecular structure.

Crystallinity affects diffusion by prohibiting diffusion through certain crystals and hindering the diffusion process. The same can be the case if a filler such as glass is used. Figure 9^{vii} gives a visual representation of this. Due to the effects that crystallinity has on diffusion, the solubility of a semicrystalline polymer can be approximated as:

Equation 3

$$S = \phi_a * S_a$$

Where:

ϕ_c = volume fraction of the polymer that is amorphous

S_a = Solubility of amorphous polymer

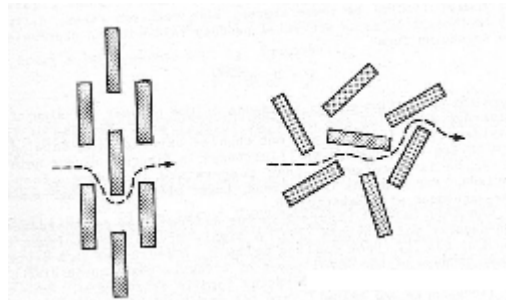


Figure 9: Crystals or Fillers Hindering Diffusion

Diffusion is affected by temperature (and transitions due to the temperature) for many reasons. One reason is that the molecules at a higher temperature contain more energy making it easier for them to overcome an activation energy barrier. This can be seen in the expression below.

Equation 4

$$D = D_0 e^{-E/(RT)}$$

Another reason pertains to the concentration of crystals. Above the melting temperature there are no crystals, but as the temperature is reduced, more crystals can form. As mentioned above, these crystals can hinder the diffusion process. This can be seen in Figure 10^{vii} (left figure) where below the melting temperature the diffusion coefficient drops faster as the temperature is reduced.

Below the glass transition temperature there are fixed microvoids, and these holes cause a dual sorption mode where the gas can be absorbed into the material or into the pores. This can be seen in Figure 10 (right figure), where below the glass transition temperature, the diffusion coefficient does not drop as quickly as the temperature is lowered.

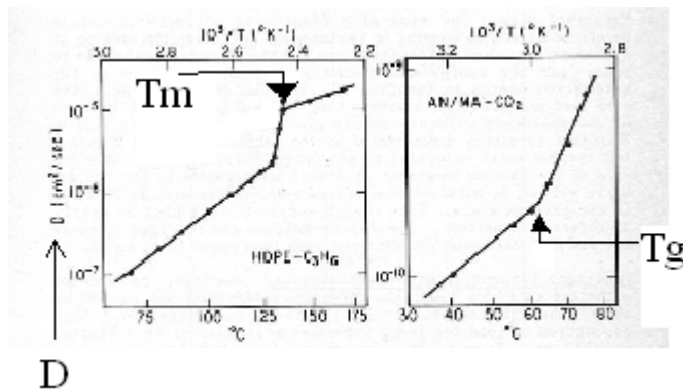


Figure 10: Ln(D) vs. 1/T data. Left plot shows how the Diffusion Coefficient changes at the melting temperature. The right plot shows how the diffusion coefficient changes at the Glass Transition Temperature.

Penetrate size and polarity also effect the diffusion coefficient. Penetrate size has an effect because more room is necessary for diffusing a larger particle through a polymer. The penetrate will need to overcome a greater activation energy. The penetrate

polarity matters as well. Only penetrate with the same polarity as the polymer it is meant to penetrate will have the ability to penetrate it well. This can be seen in Table 1^{vii} where oxygen, a non-polar penetrate, has very low permeation in the highly polar polymers in the figure.

The polymer molecular structure is expected to play a large role in the diffusion coefficient, but there is currently no general way to predict the actual affect. Consider Table 1 to see how structure can affect the diffusion process (for Oxygen as the permeate). [Note that permeability [P] relates to the diffusion coefficient [D] by the equation $P=DS$, where S is the solubility. This shows that permeability is directly proportional to the diffusion coefficient.]

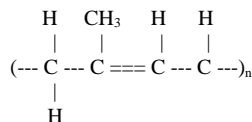
Considering Table 1, the ethylene-propylene copolymer will have very little crystallinity^{viii}, while the polypropylene (assumed to be isotactic) and high density polyethylene will have a high level of crystallinity^{viii}. The affect of this on the permeability can be seen in the figure. The permeability (and therefore the diffusion coefficient) is significantly lower for the polymers with a structure that contains higher levels of crystallinity.

Polymer type	Polymer	$P \times 10^{10}$ (cm ³ (STP) cm/cm ² scm Hg)
Olefins	Polypropylene	1.4
	Low-Density Polyethylene (Density = 0.92 g/cm ³)	3.0
	High-Density Polyethylene (Density = 0.96 g/cm ³)	0.58
	Ethylene-Propylene Elastomer	14
Rubber	Natural [-CH ₂ CH=CHCH ₂ -]	25
	Butyl [-CH ₂ -C(CH ₃) ₂ -]	1.3
	Silicone [-O-Si(CH ₃) ₂ -]	650
Highly Polar	Polyacrylonitrile	0.00025
	Poly(vinyl alcohol), dry	around 10 ⁻⁶

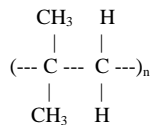
Table 1: Table showing the affects of polymer structure on permeability.

The effects of polymer structure on permeation for rubbers can be analyzed by looking at Table 1 and Figure 11^{viii}. Butyl rubber in Table 1 has a much lower permeability than Silicone. The low permeability is due to the fact that the butyl makes sluggish segment motions due to the two larger methyl side groups on every other carbon atom along the backbone. Though silicone has these two side groups on the carbon as well, it has a significantly higher permeability due to the oxygen in the backbone. The natural rubber has fewer methyl, and also has a higher permeability than butyl.

Natural Rubber:



Butyl Rubber:



Silicone:

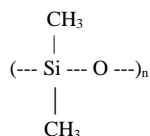


Figure 11: Molecular structure of the rubbers found in Table 1.

The three cases examined of a permeate diffusing through a polymer are a permeate diffusing through a ¹rubbery polymer, ² glassy polymer, and ³case II diffusion through a polymer. Though the derivation will not be shown, these cases were derived using Fick's laws. Any situation can be solved by finding an appropriate solution of Fick's second law^{ix}. For this reason, Fick's laws will be described below in 1-D, and

Fick's second law will be derived in 3-D. The equations for each of the three cases will not be derived from Fick's second law.

Fick's first law in one dimension (1-D) is given by:

Equation 5

$$F_x = -D \left(\frac{\partial c}{\partial x} \right)$$

Where: F_x is the flux in the x direction, which could be any single direction depending on how the axis is oriented. Flux has the units of $\frac{\text{amount}}{\text{area} * \text{time}}$. Assume the amount in the numerator to be the amount of permeate. This is not always the case since flux can occur in many different ways (ie: electrical, thermal). The area is a cross section that the permeate passes through.

D is the diffusion coefficient, which is given in units of $\frac{\text{length}^2}{\text{time}}$ (usually m²/s).

$\frac{\partial c}{\partial x}$ is the concentration gradient. It has units of $\frac{\text{amount}}{\text{volume} * \text{length}}$.

Fick's first law is only applicable in steady state diffusion. If the concentration is varying with time, Fick's second law can be used. It states:

Equation 6

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Where $\frac{\partial c}{\partial t}$ has units of $\frac{\text{Amount}}{\text{Volume} * \text{time}}$.

To better understand diffusion in three dimensions (3-D), consider Figure 12^{ix}. In this figure an element is pictured that has material flowing into the element through the

side labeled ABCD, and out of the element through the side labeled abcd. As can be seen from the figure, this means that the flux is occurring in the x-direction.

The amount of material passing through face ABCD can be calculated by multiplying the flux for face ABCD by the area of ABCD. For this calculation to work in the manner proposed, the amount of time used in the flux term must be considered as unit time. Since the units for flux are $\frac{\text{amount}}{\text{area} * \text{time}}$, when flux is multiplied by area for unit time, the end result is amount of material passing through the face of the element.

Assume there is a flux gradient in the x-direction $\left(\frac{\partial F_x}{\partial x}\right)$. At point P in the center of the

cube the flux can be F_x . This means that the flux at face ABCD is $\left[F_x - \frac{\partial F_x}{\partial x} * dx\right]$ and

the flux at face abcd is $\left[F_x + \frac{\partial F_x}{\partial x} * dx\right]$.

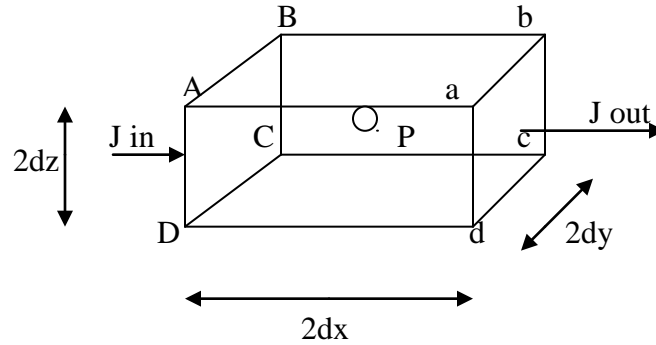


Figure 12: Image of 3-D element to visualize flux in 3-D. Point P is in the center of the element.

This means that the amount of material passing through face ABCD is

Equation 7

$$Q_{x \text{ in}} = \left[F_x - \frac{\partial F_x}{\partial x} * dx\right] * 2dy * 2dz * dx$$

Where $2dy * 2dz$ is the area of face ABCD. The amount of material passing out of face abcd is given by

Equation 8

$$Q_{x \text{ out}} = \left[F_x + \frac{\partial F_x}{\partial x} \right] * 2dy * 2dz * dx$$

The total material that is accumulating in the element is the difference between $Q_{x \text{ in}}$ and $Q_{x \text{ out}}$. When $Q_{x \text{ out}}$ is subtracted from $Q_{x \text{ in}}$, the material accumulated in the element due to the flux in the x-direction is given by:

Equation 9

$$Q_x = -8dx dy dz \frac{\partial F_x}{\partial x}$$

Quantities for the accumulated material due to flux in the y and z directions can be calculated in the same manner as it was for the x-direction, and the result will be:

Equation 10

$$Q_y = -8dx dy dz \frac{\partial F_y}{\partial y}$$

Equation 11

$$Q_z = -8dx dy dz \frac{\partial F_z}{\partial z}$$

The term $\frac{\partial c}{\partial t}$ from Fick's second law can be considered with the amount in the numerator being $Q_x + Q_y + Q_z$ and the volume in the denominator being the volume of the element ($2dx * 2dy * 2dz$). Time can be ignored because it is considered to be unity. This gives Equation 12.

Equation 12

$$\frac{\partial c}{\partial t} = \frac{Q_x + Q_y + Q_z}{8dx dy dz}$$

Since each Q term has a $(-8dx dy dz)$ term in it, this equation reduces to

Equation 13

$$\frac{\partial c}{\partial t} = - \frac{\partial F_x}{\partial x} - \frac{\partial F_y}{\partial y} - \frac{\partial F_z}{\partial z}$$

And since $F_x = -D \left(\frac{\partial c}{\partial x} \right)$, $\frac{\partial F_x}{\partial x} = -D \frac{\partial^2 c}{\partial x^2}$:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right)$$

Equation 14

Which is Fick's Second Law in 3-D^{ix}.

In order to consider a permeate diffusing in a rubbery polymer, it is necessary to have a model to predict the dependence that the diffusion has on concentration, pressure, and temperature. The most successful model is free volume theory^x.

The free volume theory can be more easily understood by considering Figure 13^x. At any temperature, the volume occupied by a unit mass of rubbery polymer is equal to the volume that is directly occupied by the polymer ("Occupied Volume" in Figure 13) plus the free volume. The free volume can be separated into two quantities, interstitial free volume and hole free volume, which can both be seen in Figure 13. The interstitial free volume is the volume which is between the molecules of polymer, and the hole free volume is the volume of holes in the material. Free volume theory assumes that the holes can be redistributed throughout the polymer (and therefore transport molecules) without an increase in free energy.

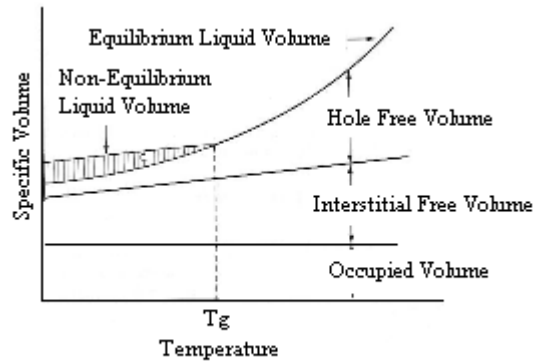


Figure 13: Specific Volume vs. Temperature plot showing Free Volume

Figure 13 shows that as a polymer's temperature is raised above T_g , the hole free volume increases at a higher rate than the interstitial free volume. While the molecule can diffuse using the voids as was voids, it can also diffuse between the molecules. A model of the process of the molecule diffusing through the "interstitial free volume" can be seen in Figure 14^x. In the normal state, while the molecule is not diffusing, the molecule is surrounded by polymer chains that are holding it in place. For the molecule to diffuse, the polymer chains need to enter the activated state where they open a pathway for the molecule to diffuse. After the diffusional jump, the polymer chains will close back around the molecule and hold it in place until another jump occurs. It should be noted that this is only one of many theories of how the diffusion takes place in a polymer.

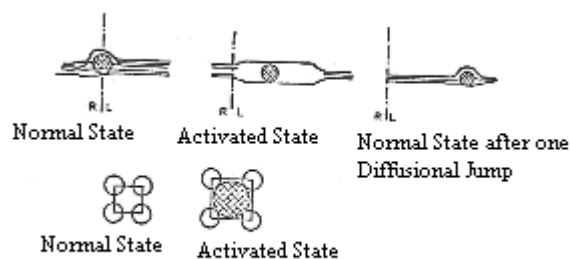


Figure 14: The DiBenedetto and Paul model for a molecule diffusing between polymer chains.

A gas diffusing in a glassy polymer will diffuse differently than it will in a rubbery polymer. This is seen in Figure 10, where the slope of the $\ln(D)$ vs. Temperature curve changes at T_g . Instead of having the holes that can be redistributed without changing the free energy (like rubbery polymers have according to free volume theory), a glassy polymer will have immobile microvoids. The gas molecules can either diffuse into the microvoids or dissolve into the bulk polymer. This is the bases for the dual sorbtion mode of a glassy polymer, which gives it a high gas solubility. The total gas concentration can be thought of as the sum of the normal sorbtion of gas into the bulk (c_D) and the sorbtion of gas into the microvoids (c_H). Therefore, the total concentration can be represented by Equation 15.

Equation 15

$$c = c_D + c_H$$

Equation 15 assumes that the gas in the microvoids is completely immobile and does not contribute to the diffusive flux. This means that Fick's first law can be given as:

Equation 16

$$F_x = -D \left(\frac{\partial c_D}{\partial x} \right)$$

and Fick's second law will be given by:

Equation 17

$$\frac{\partial}{\partial t} (c_D + c_H) = D \frac{\partial^2 c_D}{\partial x^2}$$

When polymers follow Fick's Laws, the diffusion process is known as Fickian.

To determine if the polymer is Fickian, the below equation can be considered:

Equation 18

$$M(t) = bt^n$$

Where $M(t)$ is the amount of material that has passed through the polymer in time t , b is a constant, and n can be used to determine if the diffusion process is Fickian or not. For the previous two cases discussed the n would be equal to 0.5, which makes them Fickian. There is a special “Non-Fickian” case that will now be discussed, which has an “ n ” value which is equal to 1. This case is known as Case II diffusion.

Case II diffusion occurs when organic vapors diffuse in polymers that are below the glass transition temperature. Organic vapors act as a plasticizer, and cause a polymer to swell. As the vapor diffuses through the polymer, the portion that it diffuses through has its T_g lowered so that it is rubbery instead of glassy. The portion that has not been diffused through will still be glassy. The polymer will end up having a glassy core with a rubbery shell around it as the diffusion process takes place.

There are a number of theories for how Case II diffusion takes place. In a model developed by Thomas and Windle, it is assumed that the penetrate volume fraction (ϕ) depends on time and only one spatial direction (x). The driving force for the diffusion is the difference between the concentration in the rubbery region and glassy region of the polymer. The concentration difference results in a pressure difference. This pressure difference is initially resisted by the glassy polymer chains. Eventually the solute molecules will begin penetrating into the glassy portion and the chains will relax. This will lower the pressure difference as well as the concentration difference, and the rubbery-glassy interface will move further into the polymer.

The Final case that will be discussed is polymer-polymer diffusion. The most successful method is the reptation model by deGennes^x. This model assumes that a polymer chain faces a number of obstacles as it tries to diffuse. This can be seen in Figure

15^x, where the dark line is the polymer chain, and the dots are the constraints. These dots are really other polymer molecules. The polymer can easily move along its own axis, but not perpendicular to itself. Because of this, a tube can be pictured around the polymer chain, and the tube shows the region where it can move. This tube is shown in Figure 15 by the dotted line. Because of this constraining tube, the polymer can only diffuse by reptating, which means it is slithering like a snake through the tube.

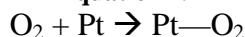


Figure 15: Model showing reptation in polymer-polymer diffusion.

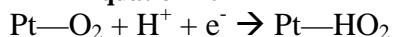
THE CATHODE CATALYST

To begin examining the cathode catalyst, the reaction at the cathode catalyst will be evaluated. To do so, the reactions that take place with platinum as the catalyst will be listed below^{xi}. The basic equation of what takes place is given in Equation 2, but the actual reactions can be more complex.

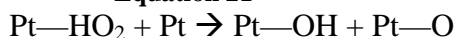
Equation 19



Equation 20



Equation 21



Equation 22



In the above set of equations, oxygen is supplied to the cathode, hydrogen ions and electrons arrive at the cathode, and the three form water (same as Equation 2) through a series of steps that occur as listed in Equation 19 through Equation 22. In Equation 19, oxygen is supplied to the cathode and it bonds with the platinum, but the O—O bond has not been broken. In Equation 20, hydrogen ions have crossed the electrolyte and electrons have arrived from the anode, and both enter the cathode. The ions and electrons bond with the oxygen that is bonded to the platinum, and form HO₂ which is bonded to platinum. The O—O bond has not been broken at this point in the set of reactions.

In Equation 21, the HO₂ which is bonded to a platinum site reacts with another platinum site. The O—O bond is broken, forming OH bonded to one platinum site, and oxygen bonded to another platinum site. In the final step, listed in Equation 22, additional hydrogen and electrons arrive and react with the OH and O which are bonded to the two platinum sites, and water is formed. This leaves the two platinum sites ready to react again. The overall reaction that takes place at the cathode (as seen in Equation 2) is called a dual site reaction because two platinum sites were used.

Vielstich considers the multiple reactions that can take place (such as those listed in Equation 19 through Equation 22) in more detail^{xii}. His research analyzed how oxygen behaves in a more complicated manner than other gasses such as hydrogen and chlorine at electrodes of platinum, gold, silver, or carbon. This is due to the extreme stability of the oxygen molecule's bond which must be broken in order for water to be formed (for the fuel cell to function correctly). He covers the potentials that correspond to the reactions, such as those listed in Equation 19 through Equation 22.

Currently, an important focus in the research on fuel cell is reducing the platinum loading. There are multiple ways of approaching the issue. These include a focus on fully utilizing the platinum that is present in the catalyst to ensure that no catalyst remains latent, alloying the platinum with another metal, or finding a different metal to use.

In H₂/air PEM fuel cells (hydrogen is supplied to the anode, air to the cathode), progress has been made to reduce the amount of platinum that is used. The loading of platinum has been reduced to around 0.6 to 0.8 mg_{Pt}/cm² (0.8 mg of platinum catalyst is applied for every cm² of cross section in the fuel cell). While this is low compared to the fuel cells of the 1990's, around a five fold reduction in the amount of platinum used in current fuel cells (in 2004) is necessary for fuel cells to be plausible for use in vehicles^{xiii}. This is due to both the cost and the amount of platinum available in the earth. The power density as it relates to the amount of platinum used must be less than 0.2 grams of platinum for every KW the cell produces when functioning at a voltage greater than or equal to 0.65V in order to meet this requirement.

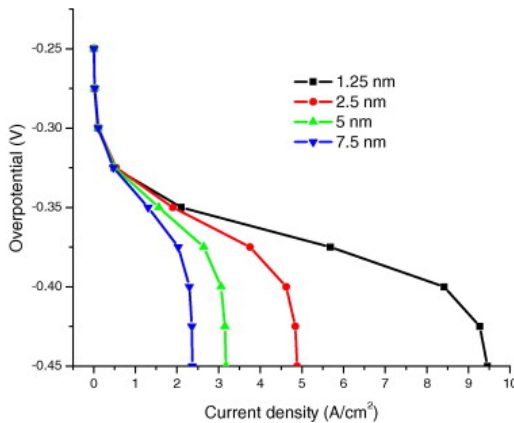


Figure 16: Plot showing the effect of particle size on losses

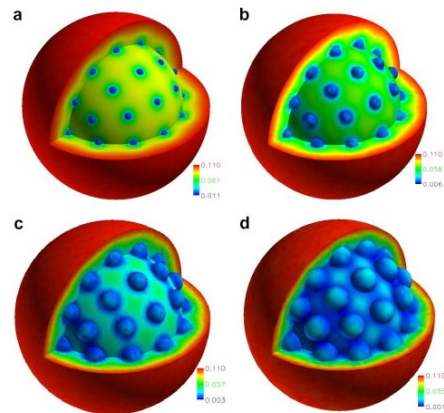


Figure 17: Figure showing effects of particle size on O₂ availability

The amount of catalyst used must be reduced at the anode and the cathode. This is not as difficult for the anode where hydrogen is supplied, because platinum is very active towards the hydrogen oxidation reaction. Platinum is not as reactive toward the oxygen reduction reaction, so while reducing the loading at the anode can be somewhat simple, reducing the loading at the cathode while keeping the same performance can be a more significant challenge.

There are two ways that the platinum loading in the cathode can be reduced^{xiii}. These are by optimizing the electrode structure so that all the platinum is effectively used, meaning that reducing the platinum loading will have kinetic affects that can easily be calculated, and alloying the platinum with another metal that is active to the oxygen reduction reaction and is compatible with PEM fuel cells (compatibility issues will be briefly discussed when non-platinum catalysts are discussed, but apply to alloys as well). The activity for some platinum alloy catalysts supported on carbon (Pt-alloy/C) is reported to be two to four times larger than the activity for Pt/C. While these results are encouraging, there are multiple issues with Pt-alloy/C catalysts which must be considered, which is why platinum alloys are not the only catalyst considered.

One of the first considerations in improving the activity of the catalyst while keeping the same platinum loading, or even reducing the platinum loading of the Pt/C that is used in current fuel cells, is by increasing the platinum's surface area. This can be done by reducing the particle size of the platinum. An example of how this can improve the performance can be seen in Figure 16^{xiv} and Figure 17^{xiv}.

As the platinum surface area increases, the performance should increase. This is because as the surface area increases, there are more sites available for the oxygen

reduction reaction to take place. Consider Figure 16 to see effects of particle size on the losses (overvoltage). At low current densities, the different particles sizes produce the same results. Around 1 A/cm^2 the different particle sizes begin performing uniquely. For the largest particle sizes (7.5nm), the current density maxes out at about 2.45 A/cm^2 . At this point the losses are severe. For the smallest particle size (1.25nm), after the current is raised past 1 A/cm^2 , the performance does decrease, but the losses only get severe after $\sim 8.5 \text{ A/cm}^2$, which is less severe than for the other particle sizes. The two sizes between 1.25nm and 7.5nm have results that land between the two.

Figure 17 shows how the particle size effects the oxygen concentration at the Pt/C. The legend for each figure shows how the color coordinates with the oxygen concentration in the figure. The feed gas has a 0.11 oxygen concentration. As can be seen in the figure, as the particle size increases, the oxygen concentration decreases significantly near the platinum. If the particle size gets too large, there is not enough oxygen present for the fuel cell to function (concentration reduces to 0.001). All the oxygen provided may not be used up, but the current will max out because the fuel in the vicinity of the platinum is depleted of oxygen.

While it may increase the performance, decreasing the particle size will not improve the catalyst performance enough to allow the loading to be reduced to the necessary level for commercial use (at least in a fuel cell car^{xiii}) while keeping the power density at an acceptable level. The catalyst needs to be improved in other ways in order to meet the requirements.

A company known as UTC developed some of the first Pt/C electrocatalysts in the 1970's. This was done in order to increase the rate of the electrode reaction as well as

lower the loading. It was proposed that the rate determining step for the Pt/C catalyst was “the dissociation of the O--O bond...”^{xiii}. By changing the spacing between the platinum atoms, it was assumed that the “strength of the Pt—O adsorption could be strengthened or weakened favorably”^{xiii}. UTC did this by alloying platinum with transition metals. A procedure was developed to form platinum alloys with high surface areas.

A description for this process, known as carbothermal reduction was developed^{xiii}. In the process, the oxide of a chosen base metal was mixed with a preformed carbon supported platinum catalyst (Pt/C), and the mixture was heated at between 800C and 1000C. In the reaction that proceeded, part of the carbon was consumed by the reduction of the metal oxide to metal, and the metal reacted with the platinum to form a platinum alloy. The mass activity (A/mg_{Pt} , the current at a certain voltage that can be achieved with a certain mass of platinum, given in mg) of these platinum alloys at 900mV were two to three times the mass activity of carbon supported platinum.

Certain specific losses should be considered to examine how the alloys improve over the current Pt/C catalyst,. The two main losses that plague the cathode are mass transport voltage losses (η_{tx}) and activation losses (η_{ORR}). By optimizing the flow field as well as the diffusion media, the η_{tx} can be reduced by 50%. By using certain Platinum-alloys, the activity could be increased by a factor of two to four. Table 2^{xiii} gives an example comparing how these improvements help the performance of the cell.

The first row shows the current performance of Pt/C as a cathode catalyst. The loading is $0.4mg_{Pt}/cm^2$, which is more than is acceptable in order to reach the necessary power density at 0.65V. The second row shows how the power density is increased when the mass transport losses are reduced. With the same platinum loading, when the mass

transport losses are cut in half, the power density raises by 200mW/cm² at 0.65V, and the grams of platinum necessary for a kW is reduced. This g_{Pt}/kW column of the table is important because the focus is to reduce the loading to 0.1 mg_{Pt}/cm² while having a performance of >=0.2g_{Pt}/kW.

Assumptions	Catalyst activity	Cathode loading (mg _{Pt} /cm ²)	P_{MEA} at 0.65 V (W/cm ²)	P_{Pt} at 0.65 V (g _{Pt} /kW)
Current performance	Standard Pt/C	0.4	0.71	0.63
50% reduced $\eta_{b,c}$	Standard Pt/C	0.4	0.91	0.48
50% reduced $\eta_{b,c}$	Standard Pt/C	0.1	0.68	0.22
50% reduced $\eta_{b,c}$	2× standard Pt/C	0.1	0.78	0.19
50% reduced $\eta_{b,c}$	4× standard Pt/C	0.1	0.91	0.17

Table 2: List of data showing how platinum loading can be reduced while keeping the power output at an acceptable level. This is done by reducing losses $\eta_{b,c}$ and/or η_{OOR} .

The third row shows the effect of reducing the platinum loading by ¼ while keeping the mass transport losses at 50%. This reduces the power density to below where it was in the original row. It is desirable to have a higher power density if possible. The g_{Pt}/kW has been brought down to 0.22, which is nearly acceptable. While there have been reports of platinum-alloy catalysts that can achieve four-fold enhancement of the activity of Pt/C, the author of Reference xiii was unable to produce these results. A two-fold enhancement was reproduced using a Pt_xCo_{1-x}/C catalyst. The fourth row of Table 2 would represent this catalyst if the mass transport could be cut in half. The power density is raised to 780mW/cm² while holding the platinum loading at 0.1mg_{Pt}/cm². For this case, the g_{Pt}/kW has been reduced to <0.2 with a catalyst loading of 0.1 g_{Pt}/cm², making it an acceptable case.

The final row of the table shows how a four fold enhancement of the activity would affect the power density. While these results look optimal, the fifth row results are not believed to be obtainable with current fuel cell technology^{xiii}.

One of the hypotheses on how alloying can improve activity is by introducing a metal that is smaller than platinum. When this is done, it substituted into the lattice for platinum, which causes the lattice parameter to contract. This causes the Pt-Pt interatomic bond distance to be reduced, which results in more favorable sites for the oxygen.

A second hypothesis is that the surface is roughened because the base metal that is alloyed is leached off. This causes an increase in surface area, which causes an increase in performance.

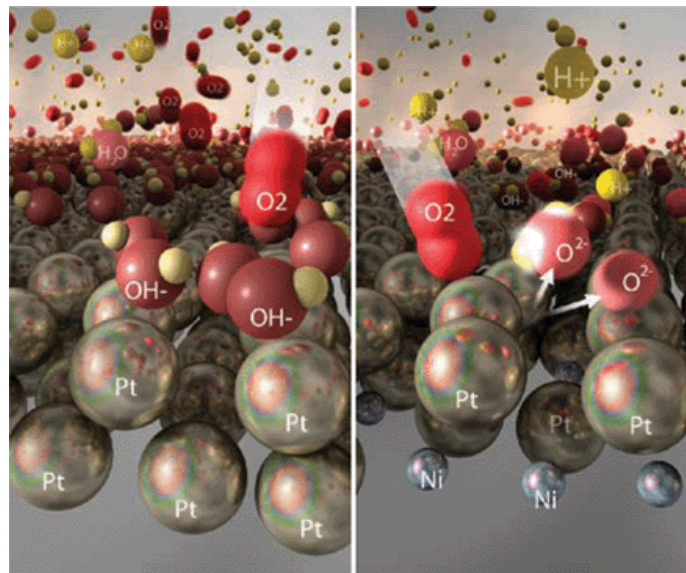


Figure 18: On Left-shows how hydroxide molecules can block the oxygen from getting to the platinum. On Right- shows how nickel is alloyed and no hydroxide is present.

Another hypothesis, which came from a study of Pt_3Co -alloys, is that the alloying inhibits OH adsorption on the platinum. The OH adsorption can be an issue for the catalyst^{xv}. In the cathode, charged oxygen atoms can react with protons to form

hydroxide molecules. These molecules are attracted to the platinum and can eventually pull the platinum off the surface. Over time, this will affect the fuel cell in a negative way. An example of this hydroxide problem, and the counter-effect of alloying, can be seen in Figure 18^{xv}.

While creating platinum alloys can help the performance of a fuel cell and bring the platinum loading down to a level that is acceptable, some of the concerns associated with platinum alloys should be considered. PEMFCs have more issues with the platinum catalyst than other fuel cells such as PAFCs (phosphoric acid fuel cell) because^{xiii}:

- a) The operating temperature of a PEMFC can be around 65-95C. Since this temperature is low it can cause the electrochemical reactions to be sluggish.
- b) The anion adsorption on the catalyst (i.e.: the adsorption of the oxygen onto

the platinum) is significantly lower than in phosphoric acid or sulfuric acid fuel cell.

- c) The membrane in the cell is a thin ionic membrane that measures around 25 micrometers in thickness. The ionomer membrane has only about 1/10 of the number of

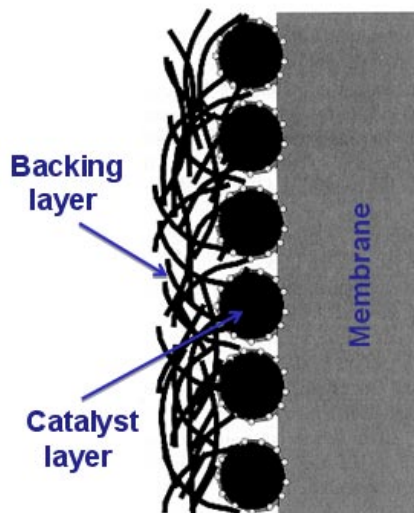


Figure 19: The catalyst layer.

available H^+ sites in a PAFC (these sights are what the ions use to conduct across the membrane). Because of this lower number of sites, the membrane is

much more susceptible to contamination, and this contamination can be caused by the metal that is alloyed to platinum.

- d) The catalyst layer also contains the ionomer which the electrolyte membrane is composed of. The layer depends on this ionomer to conduct the ions from the electrolyte to the catalyst, and since less ionomer is in the electrode, it is more susceptible to contamination.

Figure 19^{xvi} shows this catalyst

layer. In the figure, the backing layer is the carbon cloth or carbon paper (the GDL, or gas diffusion layer), the large black circles are the carbon support, the little white circles are the platinum on the carbon support, and the membrane is

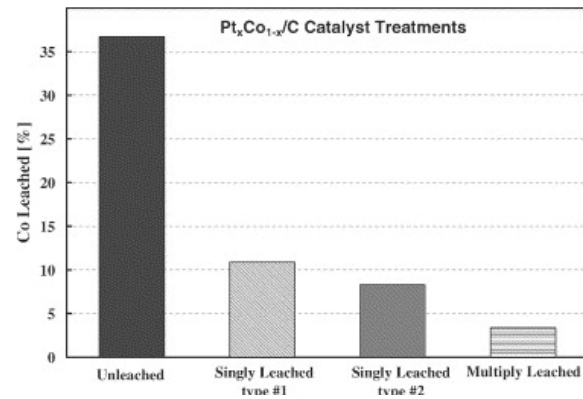


Figure 20: Figure showing the effects of pre-leeching.

the electrolyte. Though it is hard to see, there is a thin gray coating on the carbon

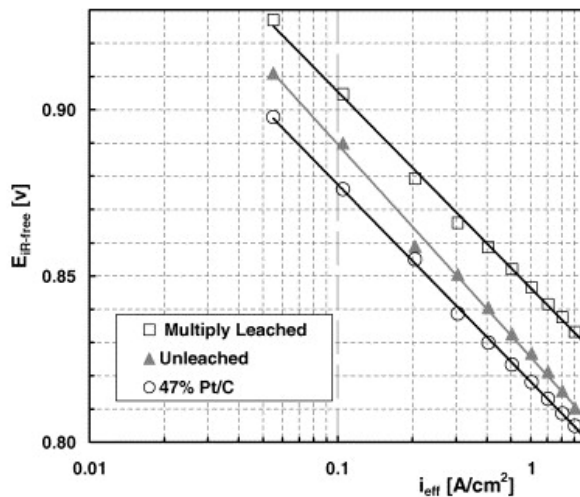


Figure 21: Plot showing the effects of leeching

were mentioned above involved contamination of the ionomer, which is in both the

electrolyte and the catalyst ink. By alloying the platinum, another metal is introduced into

supported platinum in the figure. This thin coating shows the ionomer in the catalyst ink which is used to transfer the ions from the membrane, while the carbon support transfers the electrons from the carbon cloth.

Two of the four problems that

the fuel cell, and the metal can be susceptible to leaching, which can cause the metal to contaminate the ionomer. When the base metal is present in a form not bonded to platinum, it is called leaching of the base metal. There are multiple problems that can be caused by this leaching, some of which are listed below^{xiii}.

The first problem is that the conductivity of the ionomer can be reduced due to dehydration because the base metal cations are replacing the hydrogen cations which are used for conduction. A second problem is that oxygen can have a hard time diffusing through the ionomer in the catalyst in order to get to the platinum alloy. The final problem is that certain base metals, such as iron and titanium, can degrade the membrane. To reduce the leaching issues which is caused by the presence of the base metal, pre-leaching of the alloy has been proposed.

There are three possible causes of the leaching^{xiii}. The first is that there can be an excess amount of the base metal used in the preparation of the platinum alloy. Secondly, there can be incomplete alloying, even if excess base metal is not used. This can be due to low alloying temperature during the formation of the alloy. Lastly, since the base metals are thermodynamically unstable under the PEMFC working conditions (the PEM potential in acidic electrolytes), even if the platinum alloy is well made, it can still leach out.

Alloys that were pre-leached have been tested^{xiii} (in a process called multiply pre-leaching where a batch can be pre-leached) and compared with alloys that were not pre-leached, as well as results from Pt/C. Figure 20^{xiii} and Figure 21^{xiii} show the results. Figure 20 compared the amount of base metal that has leached (this is why Pt/C is not included in this figure, since there is no alloy base metal in Pt/C). The unleached

platinum alloy has 37% of the cobalt (which is the base metal that is alloyed for the $\text{Pt}_x\text{Co}_{1-x}/\text{C}$ alloy) leached off. For the multiply leached method, only around 4% of the cobalt had leached off. A 4% leaching means that ~16% of the H^+ sites in the electrode ionomer (catalyst ink, not the electrolyte) will be replaced with cobalt, which is acceptable. However, the 37% leaching is too high. This amount of cobalt could replace all of the H^+ sites in the electrode.

Figure 21 shows the results of tests that took place in a fuel cell. As can be seen, the unleached platinum alloy performed better than the Pt/C at low current densities, but as the current is increased, the Pt/C's performance surpasses that of the unleached platinum. The pre-leached platinum alloy performs much better at the lowest current density, and it appears to have a smaller negative slope, so its overall performance is the best.

In order for platinum alloys to be used in future fuel cells, a few issues need to be resolved. The leaching issue needs to be corrected, but it can be resolved by using the multiply pre-leaching technique^{xiii}. The carbon supported platinum alloy needs an improved electrochemical surface area, which will help to lower the platinum alloy loading. Lastly, the mass transfer in the catalyst needs to be improved so η_{L} can be reduced by 50% to obtain the results shown in Table 1. This reducing of the mass transport losses needs to be accomplished for any cathode regardless of the catalyst.

One last category of cathode catalyst should be considered, it is the platinum free catalyst. This can be a difficult topic for PEMFCs, because the acidity in the cell rules out non-noble metals and perhaps all oxides. The two transition metals that are commonly considered are iron and cobalt.

For platinum free catalysts, the support needs to be considered as well. In some cases, instead of using a carbon supports like the platinum and platinum alloy catalysts considered before (Pt/C or PtCo/C), a new support should be considered. Some of the types of carbon supports used for the platinum free catalyst are obtained through specific polymerization techniques. Two of the catalysts are iron phthalocyanine and cobalt methoxytetraphenylporphyrin.

The topic of platinum free catalysts is very interesting because a completely new question arises: If this new catalyst is basically free and readily available in the environment, how much can be used in a fuel cell? While the focus was on reducing the loading of the catalyst, with a platinum free catalyst the loading is not an issue. A higher loading must be considered because the performance of these platinum free catalysts is generally much worse than the performance of platinum catalysts. While utilizing a platinum free catalyst may be viable option, the amount of catalyst necessary may be so huge that the cell cross section needs to be increased, and by doing so, the weight will increase, and more ionic conducting membrane (as well as the bipolar plates and other potentially expensive components) need(s) to be used. In the end, this can end up costing more than the Pt/C or Pt-alloy/C catalyst fuel cell did.

In order to compare catalysts (i.e. comparing non-platinum to platinum-alloys or non-platinum to non-platinum catalysts), two factors should be considered. These factors are the turnover frequency and the volumetric site density. The turnover frequency evaluates how many electrons are transferred for each active site of the catalyst per second. If an iron catalyst is considered, the turnover frequency would be given as: $\#e^- / (\text{Fe s})$. The volumetric site density evaluates how many active sites are present in a

certain volume of catalyst (active sites/cm³). Once the turnover frequency (T.O.F) and the volumetric site density (S.D) are obtained, other information, such as the current density or the current per volume, can be found. The equations to do so are listed in Equation 23 and Equation 24, where e^- is the charge of an electron, 1.6E-19C, and t is the thickness of the catalyst layer.

Equation 23

$$\text{Current Density, } i = e^- * \text{T.O.F.} * \text{S.D.} * t$$

Equation 24

$$\text{Current per Volume} = e^- * \text{T.O.F.} * \text{S.D.}$$

Faubert's catalyst is considered to have the best documented performance of any non-platinum catalyst^{xiii} (2004). His tests were performed on a 1cm² H₂/O₂ PEM fuel cell at 327K using iron as the catalyst. At 800mV, the cell had a current density of 38mA/cm². The carbon support that was used was pyrolyzed perylenetetracarboxylic dianhydride (PTCDA). This support was used to increase the S.D.. While the non-platinum catalysts used and referenced by reference xiii were most commonly supported by non traditional carbon (an example of traditional carbon is Vulcan XC-72R carbon), there are other sources^{xvii} that use carbon black, so it should not be assumed that what reference xiii mentions is the only way of supporting non-platinum catalysts.

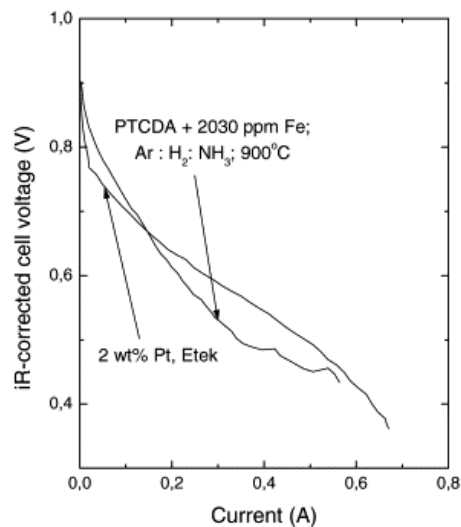


Figure 22: Figure from work done by Faubert which compares non-Pt to low loading Pt catalyst

On the PTCDA support, a catalyst layer containing 1.6E17 atoms of iron was possible. A T.O.F. of 1.7 e⁻/(Fe s) for the Fe/PTCDA was obtained. This is only around

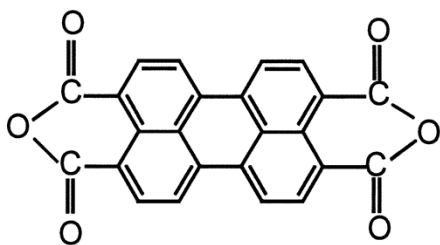


Figure 23: The molecular structure of PTCDA

1/15th of the T.O.F. of industrial platinum. The S.D.

was calculated to be $9 \times 10^{18} \text{ Fe/cm}^3$, which is only

$1/35^{\text{th}}$ of that of documented platinum catalysts.

This S.D. was limited by the number of nitrogen

sites for the iron to attach to on the PTCDA. The

performance of the non-platinum catalyst tested by Faubert is plotted in Figure 22^{xiii}, and shows how it compares to a previously tested 2% Pt/C.

The molecular structure of PTCDA is shown in Figure 23^{xvii}. The electrocatalyst is obtained by combining transition metal salts such as iron and a source of nitrogen adsorbed on a high surface carbon (such as PTCDA)^{xviii}. There are four ingredients that are necessary to make a non-platinum oxygen reduction electrocatalyst^{xviii}. These ingredients are listed below:

- 1) A transition metal such as Fe, Co, or Cr
- 2) A source of nitrogen
- 3) A source of carbon
- 4) A high temperature heat treatment ($\geq 800^\circ\text{C}$)

The nitrogen can come in any of three forms. It can be a nitrogen containing solid adsorbed with the metal precursor, nitrogen groups on a modified carbon support, or a nitrogen containing gas introduced in the reactor.

Reference xiii considers all that would be necessary for the non-platinum catalyst to be feasible. With a carbon loading of 0.4 mg/cm^2 , a catalyst layer thickness of ten micrometers is obtained. If a high surface area, conductive material could be formed which retains all of the nitrogen in the proper configuration, and if an iron could be

coordinated into each of these nitrogen sites, then if each site had access to adequate paths for conducting electrons, hydrogen ions, and oxygen, a maximum active site density of 1.3×10^{21} sites/cm³ could theoretically be achieved. If the previously mentioned T.O.F. of $1.7 \text{ e}^-/(\text{Fe s})$ was true for this catalyst, then the current density could be as high as 350 A/cm^3 , which is adequate for commercial use in a fuel cell car.

This theoretical data is only hypothesizing about a catalyst that had not been made. Not only does the catalyst need to be made, but it needs to continue functioning well, and the catalyst itself needs to not cause problems for the rest of the cell.

Even if the non-platinum catalyst could perform well enough, it also has to avoid corrosion problems due to the metal being in an acidic medium (this can be an issue for alloys as well), and the oxygen reduction reaction (ORR) needs to occur correctly. An example of the ORR not taking place correctly can be observed by the fact that iron catalysts have a tendency to reduce oxygen to hydrogen peroxide rather than water. Hydrogen peroxide is known to chemically degrade the ionic membrane of a PEM fuel cell. This is a significant issue since the current best non-platinum catalyst is iron.

While it would be the optimal situation for non-platinum catalysts to replace platinum catalyst in fuel cells to reduce the cost as well as remove the dependence on a limited resource, it is a very difficult task to achieve. There are many “if” scenarios, and unlike with platinum-alloy catalysts, the work that has been done is primarily speculation rather than substantial data.

THE ANODE CATALYST

It should be noted that many of the factors that affect the cathode catalyst directly apply to the anode catalyst as well (i.e.: particle size). For the anode catalyst, two different cases may be considered. These cases involve using hydrogen or formic acid as the fuel. In either case, hydrogen is what crosses the electrolyte and is actually being used to generate power from the cell. Everything else in the fuel produces exhaust that is released from the anode.

The reactions that take place in a fuel cell using hydrogen as the fuel have already been discussed, so the reactions in a cell using formic acid will now be considered. When formic acid is used, the hydrogen in the acid is utilized to power the cell. Formic acid has the composition HCOOH , and the catalyst must break the bonds to form some combination of H , CO_2 , and/or CO . This extra step of breaking the bonds in the formic acid takes extra energy, which means that a formic acid fuel cell will never theoretically be as efficient as a hydrogen fuel cell.

Formic acid is used as a fuel because it is considered safe to transfer and handle. Formic acid is in liquid form, unlike hydrogen, so it does not need to be contained in a pressurized vessel. Formic acid is safe, and when dilute at room temperature, it is considered by the US Food and Drug Administration as a food additive that is generally safe^{xix}.

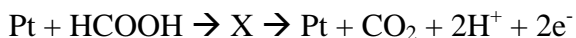
The reason formic acid would be considered over methanol, which is the other common liquid fuel used in PEM fuel cells, is because of the potential advantages it has.

One of these advantages is that formic acid has a much smaller crossover flux through Nafion than methanol does.

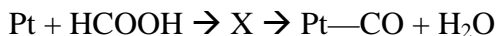
When formic acid is used as the fuel, the catalyst can be poisoned. This is the case for platinum, which is the most common catalyst used in fuel cells. When a formic acid fuel cell uses platinum as the anode catalyst, there are two reactions that can occur.

Consider the below reaction equations^{xix}:

Equation 25
Formic Acid Oxidized by Pt Directly into CO₂:



Equation 26
Formic Acid Oxidized by Pt to CO:

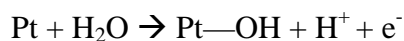


The desired reaction is given in Equation 25, where CO₂ is formed. This CO₂ will flow out of the system as exhaust on the anode side. If this was the only reaction that could take place, platinum would be an acceptable catalyst for formic acid fuel cells.

The second reaction, given in Equation 26, can cause significant problems for the fuel cell. When CO is present, a bond between the platinum and the CO is formed (Pt—CO). Because of this bond, reactions can no longer take place at the platinum site that has been bonded to. This bonding of the CO to the platinum site is the poisoning of the cell taking place. As more CO bonds to the active platinum sites, the cell performance will continually degrade, until the cell does not function.

Both of these reactions (Equation 25 and Equation 26) have an equal chance of occurring. There are other reactions that can take place that will fix the poisoning issue. The reactions are listed below in Equation 27 and Equation 28:

Equation 27
Water Activation Reaction



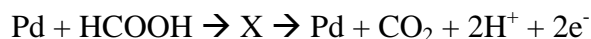
Equation 28
Recycling on Platinum Reaction



The combination of Equation 27 and Equation 28 will cause the poisoned platinum to react again in the cell.

The University of Illinois has performed research on formic acid fuel cells, and found that palladium catalysts can help to avoid the poisoning issues of the anode^{xix}. Equation 29 shows the only reaction that takes place when palladium is used as the catalyst.

Equation 29
Formic Acid Oxidized by Pd into CO₂:



Formic acid has not been considered as a fuel for PEMFCs for as long as methanol has been because of the poisoning of the platinum. It was not until palladium

was used as a catalyst that formic acid seemed a viable option. With palladium (or a palladium alloy), formic acid fuel cells may be the next step in liquid fueled cells.

There is another advantage to using palladium over platinum, this is the fact that palladium is cheaper. When compared to a metal like silver, it is still very expensive, but when compared to platinum, it is around five times cheaper. The cost of platinum, palladium, and silver over the last year can be seen in Figure 24 through Figure 26ⁱ.

While silver alone is not a common anode catalyst, it is included to show a comparison to a common metal.

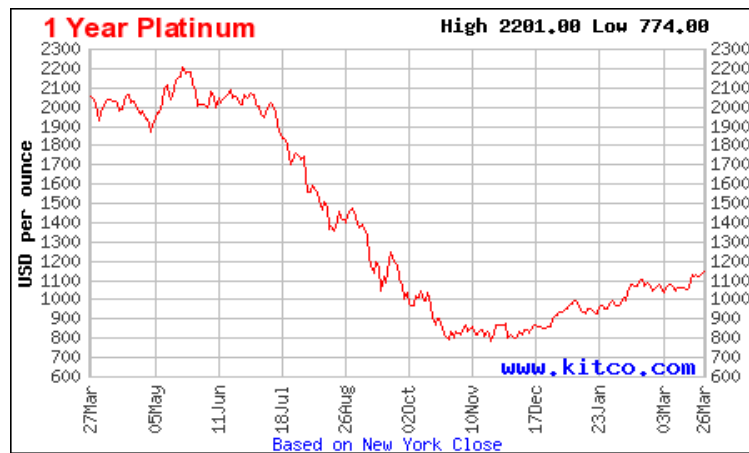


Figure 24: Price of platinum per ounce from March 27, 2008 to March 26, 2009

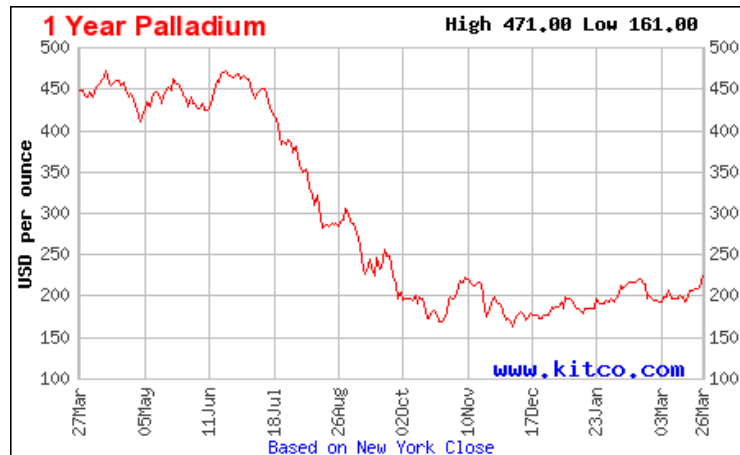


Figure 25: Price of palladium per ounce from March 27, 2008 to March 26, 2009



Figure 26: Price of silver per ounce from March 27, 2008 to March 26, 2009

HOT PRESSING THE MEA

The membrane electrode assembly (MEA) is the heart of the fuel cell. It consists of the electrolyte (usually a thin sheet of Nafion), as well as a cathode and anode gas diffusion electrode (GDE). The GDE consists of a gas diffusion layer (GDL), as well as the catalyst which is commonly painted onto the GDL in ink form (the catalyst can also

be painted onto the electrolyte). The GDL is commonly either carbon paper or carbon cloth. The function of the GDL is to transfer electrons.

The MEA is hot pressed to ensure that the components have intimate contact with one another. This allows the MEA, and the fuel cell as a whole, to work more efficiently. In depth research was performed^{xx} to find the optimal hot pressing conditions for the MEA. Three factors were considered which affect the overall performance of the cell after pressing^{xx}. These three factors were

a) The temperature that the MEA is pressed at.

b) The pressure that the MEA is pressed at.

c) The amount of time that the MEA is pressed for.

For each factor, three types of tests were performed, and the results are given in three

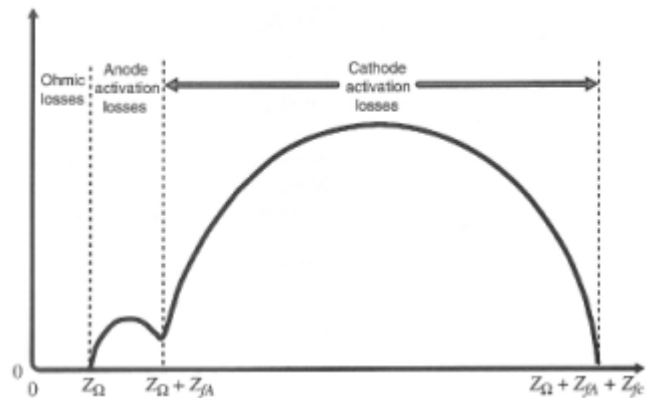


Figure 27: Example of a Nyquist Plot

different plots (a plot of the change in power density over time, a polarization plot, and a Nyquist plot). While the plot of the change in power density over time is self-explanatory, the polarization plot and the Nyquist plot will be described below.

A polarization plot can be seen in Figure 1. A polarization plot shows how the voltage changes as the current is changed. The change in the voltage as the power density (or power) is changed is often included on a polarization plot as well.

A Nyquist plot is pictured in Figure 27ⁱⁱ. The Nyquist plot shows the losses that are present in the different zones indicated on the plot. A Nyquist plot gives more detailed

information about the activation losses than the polarization plot because it shows the losses at the cathode and the anode separately. On a real Nyquist plot (as opposed to Figure 27), there are not commonly two points where the slope is zero, but one point. The shape of the plots will appear to lean to the right due to the anode activation loss.

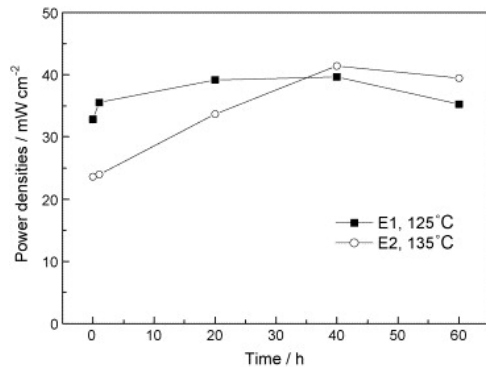


Figure 28: Change in Power Density with time for MEAs pressed at two different temperatures.

When hot pressing is performed well, it can increase the performance of the cell greatly for liquid fed fuel cells. However, if the procedure is performed poorly, it can cause the MEA to be ruined. A way this can happen is when the electrolyte is dehydrated by poor pressing procedures.

Liquid fed fuel cells (i.e.: formic acid and methanol fuel cells) are affected in a much greater way than hydrogen fuel cells by the pressing procedure. Hot pressing affects the liquid fed cells because there is liquid, as well as CO_2 forming, at the anode, and water is forming at the cathode. Having these present can separate the catalyst from the electrolyte membrane which will deteriorate the performance of the cell greatly.

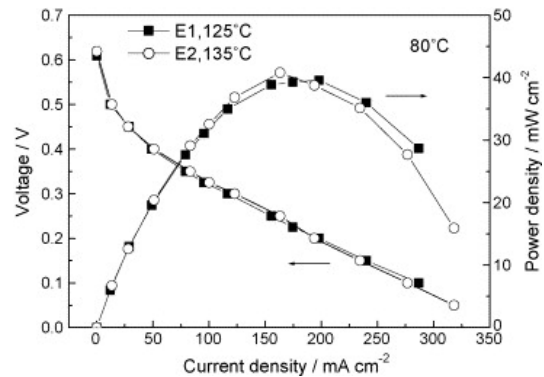


Figure 29: Polarization Plot from test performed at 80°C on MEAs prepared at two different temperatures

The first factor considered is at what temperature the MEA is pressed. Reference xx performed tests at two different temperatures (125C and 135C). Figure 28 shows the plot of how the power density changes over time for these two samples.

Initially, the MEA that was pressed at 125C performs better. After about 40 hours, the MEA that was pressed at 135C has a better performance, and the performance of the MEA pressed at 125C begins decreasing rapidly.

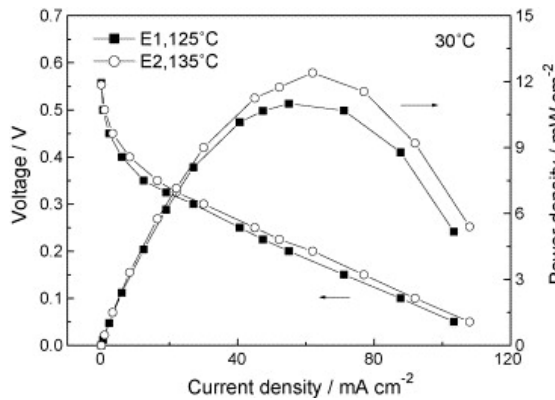


Figure 32: Polarization Plot from test performed at 30C on MEAs prepared at two different temperatures

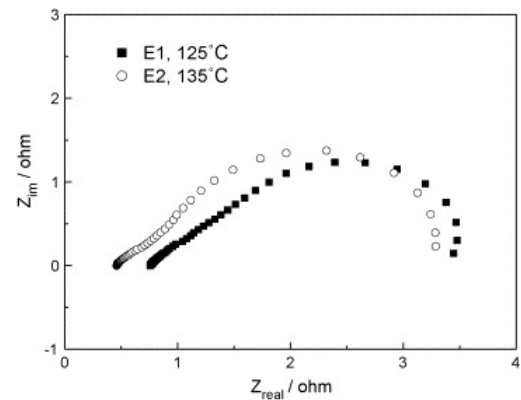


Figure 31: Nyquist Plot for MEAs prepared at 2 different temperatures

It is believed that since the pore size (in the electrolyte) and the mass transport rate decrease when the MEA is pressed, the MEA pressed at a higher temperature is affected to a higher degree. This causes it to take longer for the MEA to be conditioned completely. Because

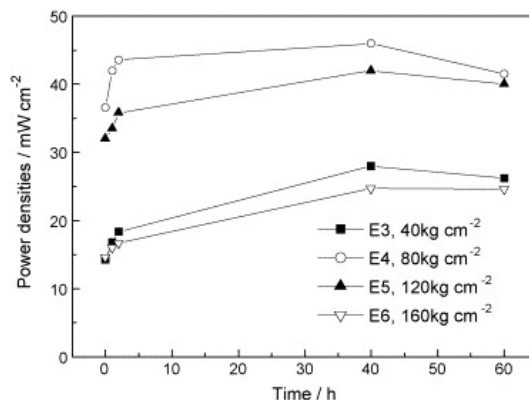


Figure 30: Change in Power Density with time for MEAs pressed at four different pressures.

the MEA pressed at a lower temperature was not compressed as much, the liquid (as well as the CO₂ and water formed) will have an easier time washing the catalyst away. This is the cause of the degradation of performance after 40 hours.

A Polarization plot is shown in Figure

29^{xx} for the two temperatures at which the

MEAs were pressed. These results were obtained when a cell was run at 80C. The sample that was pressed at 135C had a higher maximum power density. This is because of the

poor contact between the electrodes and the electrolyte due to a lower pressing temperature which led to a slightly lower performance for the MEA pressed at 125C.

When the cell temperature was decreased to 30C, the difference in the performance of the two samples becomes more significant. This can be seen in Figure 30^{xx}. As can be seen in the figure, the MEA pressed at 135C outperforms the MEA pressed at 125 C throughout the entire current range.

The Nyquist plot comparing the two samples is given in Figure 31^{xx}. The ohmic losses for the sample pressed at 135C are nearly half of what the losses are for the MEA pressed at 135C. Additionally, the overall losses are less for the MEA pressed at 135C.

By examining the given data, it would seem that the MEA performs better when pressed at a higher temperature. There is obviously a limit to how high the temperature can be because the membrane must not be damaged.

The next factor to be considered will be the hot pressing pressure. For this test, four samples are considered. These are samples that were pressed at 40kg/cm², 80 kg/cm², 120 kg/cm², and 160 kg/cm².

Figure 32^{xx} shows the plot of the change in power density over time.

The plot shows that the MEAs pressed at 1100psi and 1650psi (80kg/cm² and 120kg/cm²) performed much better than the other two that were tested, and of these two, the

MEA pressed at 1100psi performed the best. It should be noted, however, that for long

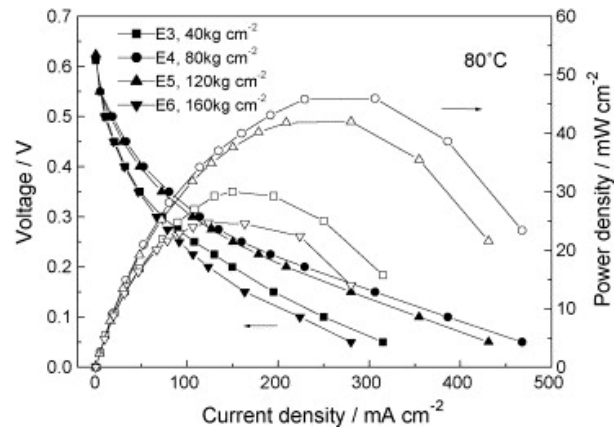


Figure 33: Polarization Plot from test performed at 80C on MEAs prepared at four different pressures

range testing, the MEA pressed at 1650psi will most likely have the best performance.

This is deduced from the fact that at 60 hours, the MEA pressed at 1100psi has a negative slope with a greater magnitude than that of the MEA pressed at 1600psi.

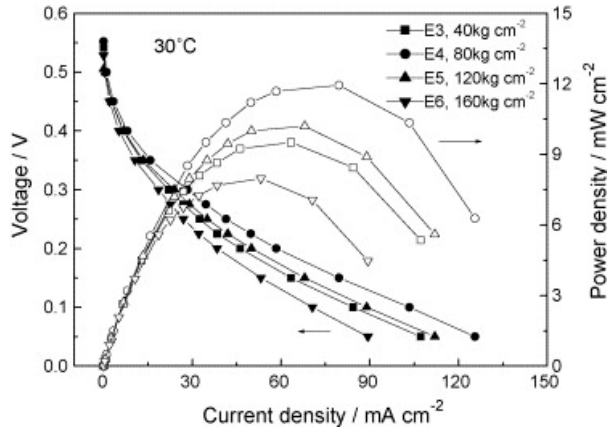


Figure 34: Polarization Plot from test performed at 30°C on MEAs prepared at four different pressures

margin (Figure 34^{xx}).

The polarization plot for the test performed at 80°C (Figure 33^{xx}) shows that even at high temperatures, the MEA pressed at 1100psi shows a considerable advantage over the other three samples. At 30°C, the polarization plot shows that the sample pressed at 1100psi outperforms the other samples by a wide

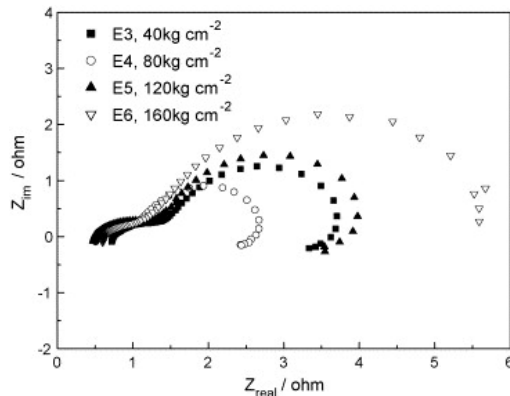


Figure 35: Nyquist Plot for MEAs prepared at four different pressures

The Nyquist plot for the four samples can be seen in Figure 35. This figure gives a good indication that the hot pressing pressure affects the cathode activation losses more than the pressing temperature does. It can be seen in the plot that the sample pressed at 1100psi

performed better than the other samples (it had much less activation loss at the cathode), and

that the sample pressed at the highest pressure incurred much greater losses in the cathode because of it.

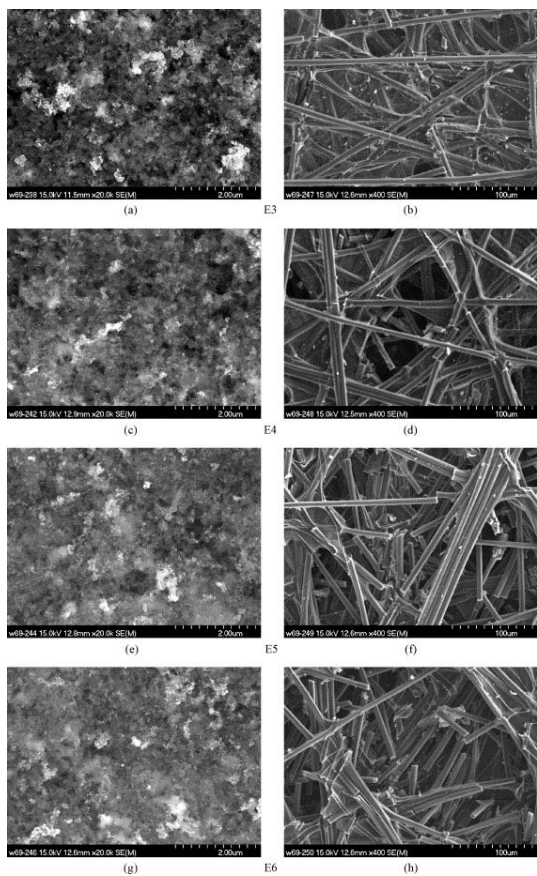


Figure 36: SEM photos of anode catalyst after being pressed at 550psi, 1100psi, 1650psi, and 2200psi.

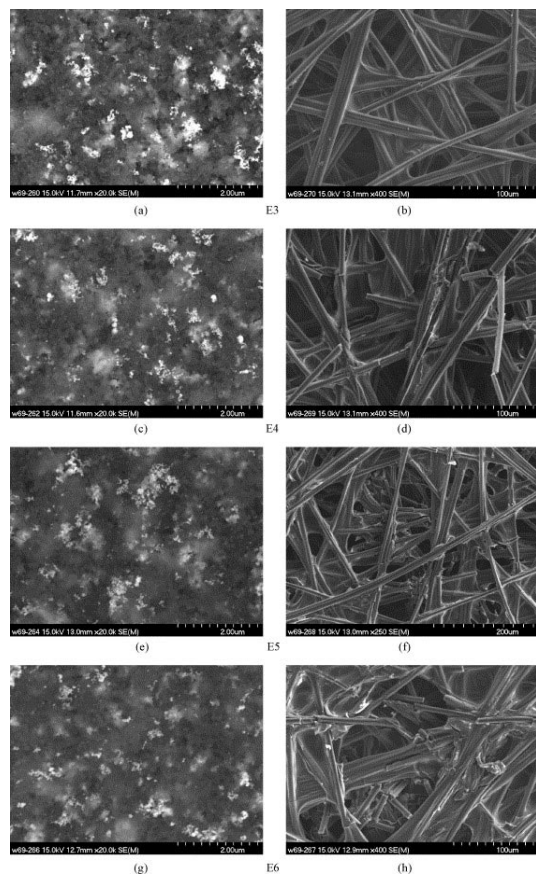


Figure 37: SEM photos of cathode catalyst after being pressed at 550psi, 1100psi, 1650psi, and 2200psi.

A new factor is introduced for examination when the pressing pressure is considered. This factor is how the catalyst layer and the carbon backing (GDE) are affected by the pressures applied. Figure 36^{xx} and Figure 37^{xx} show SEM images of the anode and cathode respectively.

The left column of each figure is made up of photos of the catalyst layer (from top image to bottom image, samples are 550psi, 1100psi, 1650psi, and 2200psi), and the right hand column is composed of photos of the carbon backing (GDE). As the pressure is raised, the catalyst layer is more compressed, and becomes less permeable. At high pressures, the carbon in the GDE begins to break. When the carbon in the GDE breaks down, some of the electronic pathways in the GDE are destroyed, which causes ohmic resistance. These two factors indicate why increasing the pressure too much can cause an MEA to perform worse.

The final factor to be considered is the hot pressing time. Three times are considered: 50s, 90s, and 180s.

The plot showing how the power density changes with time is given in Figure 38^{xx}. Each of the samples have a nearly identical profile. The sample pressed for 90 seconds shows the best performance over the 60 hour test.

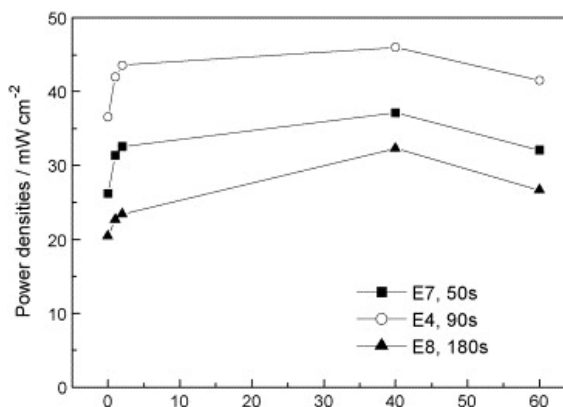


Figure 38: Change in Power Density with time for MEAs pressed for three different lengths of time

The polarization curve at 80C for the three different temperatures is given in Figure 40^{xx}. The sample pressed for 90 seconds performs better than the other samples

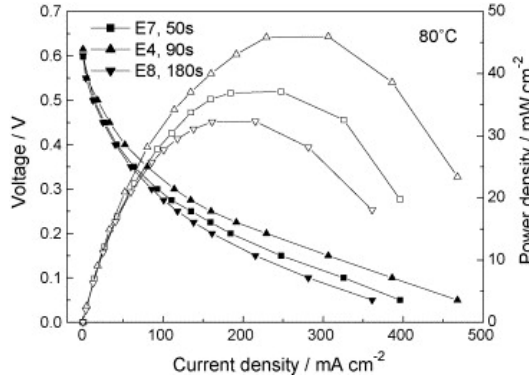


Figure 39: Polarization Plot from test performed at 80C on MEAs prepared for three different lengths of time

when tested at 80C. The polarization curve at 30C for the three samples is shown in

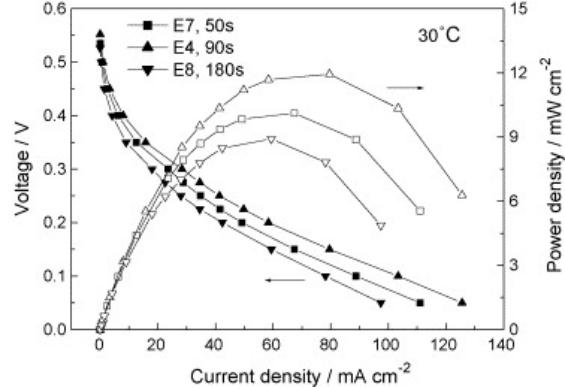


Figure 40: Polarization Plot from test performed at 30C on MEAs prepared for three different lengths of time

Figure 39^{xx}. Once again, the sample pressed for 90 seconds shows the best performance.

The Nyquist plot for these three samples is given in Figure 41^{xx}. The samples pressed for 90 and 180 seconds have relatively the same ohmic losses, but the cathode activation losses experienced by the sample pressed for 180 seconds are much more significant than those for the sample pressed for 90 seconds. The sample pressed for 90 seconds had the best performance.

The change in performance caused by the variation in MEA hot pressing time are due to contact resistance and compression of the electrolyte. When the MEA is not hot pressed for long enough (50 seconds), there is not good contact between the electrolyte and the catalyst layer. This causes contact resistance

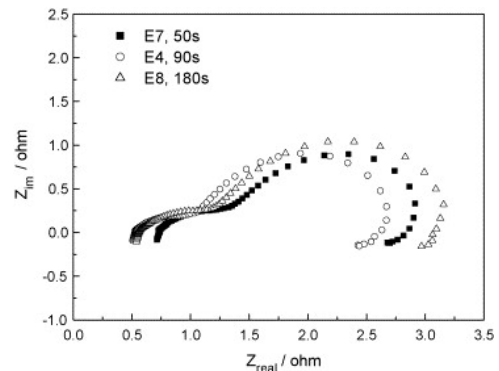


Figure 41: Nyquist Plot for MEAs pressed for three different lengths of time.

(ohmic losses), which leads to the poor performance of the MEA. When pressed for too long (180 seconds), the electrolyte is compressed too much, and porosity and mass transport issues arise.

III. EXPERIMENTS

TESTING FUEL CELL HARDWARE:

The initial stage of the project was completed with purchased fuel cell hardware. Cell housing that was custom made to be used with formic acid was purchased from Fuel Cell Technologies. To test the housing, two MEAs were purchased from <http://fuelcellstore.com> (Methanol Fuel Cell MEA with GDL (“5L SP-DMFC MEA 5cm²)). No conditioning was performed on these MEAs (at the time of initial testing, the importance of conditioning was not apparent).

The data obtained from the tests using 3M and 5M formic acid was far below the desired performance. Extensive testing was performed, but results did not improve. Since the anode and cathode catalysts were platinum based (Pt/C, PtRu/C), it was determined that a palladium based anode catalyst should be prepared in house. A palladium based catalyst was deemed necessary due to the poisoning that occurs to a platinum catalyst used with formic acid.

FORMULATING PD/C:

The first method for preparing Pd/C was a microwave assisted polyol method. This method uses ethylene glycol to uniformly heat a mixture of PdCl₂, Carbon, and

KOH. One of the byproducts of the reaction that takes place is Pd/C. This byproduct can be filtered out of the solution after the microwave heating process takes place.

An ink was prepared using the Pd/C that was formulated. The process used for making the ink involved magnetically stirring Pd/C, water, Isopropanol, and 5wt% Nafion solution. Once the ink was made, it was painted onto the carbon paper at room temperature; only a single layer was painted on. This method did not result in a catalyst with an acceptable performance because the Pd/C was not well distributed in the ink (the importance of stirring the ink thoroughly was not yet established) and an uneven distribution of the ink on the carbon resulted from the single layer application.

There were many problems with the above mentioned procedure. Not only did the microwave assisted polyol process not produce good results (even when the ink was prepared correctly and painted on in an acceptable fashion in future tests), but the stirring method was wrong and the painting procedure was impractical. Many catalysts were prepared in this manner, and a current could not be drawn from a cell using these catalysts due to the preparation method.

Because of the poor results when using the microwave assisted polyol process, research was done to find another method for producing Pd/C. The method that was decided upon was a sodium borohydride reduction reaction method from Reference xix. In this method, a solution of 100mL of water and 60mg of carbon (Cabot Vulcan XC-72R) is sonicated for three minutes. After this stirring procedure, 1.33 grams of a 5wt% solution of PdCl₂ is added to the solution. A solution of 10ml of water and 100mg of sodium borohydride is prepared and immediately added drop wise to the solution while

the solution is being stirred vigorously. Finally, enough sodium hydroxide is added to the solution to bring the solution to a pH of 11.

The solution is then stirred vigorously for one hour, and allowed to settle for half an hour. The solution is filtered and allowed to sit overnight, approximately 16-20 hours (this is done because the filter allows the carbon to pass through it if the resulting Pd/C is immediately rinsed with water). After the solution has filtered and sat, the Pd/C is rinsed with water. The resulting Pd/C is allowed to set in an oven approximately 16-20 hours at 90C.

MAKING A CATALYST INK AND APPLYING IT TO A GDE:

An ink is formed with Pd/C through the following procedure. In a 10ml beaker, 60mg of Pd/C is added to a solution of 350mg of water, 750mg of isopropanol, and 100mg of 5wt% Nafion solution. The solution is sonicated for two minutes. During the stirring procedure, the 10ml beaker sits in a tray filled with ice water to keep the solution from overheating.

A 5cm² piece of carbon paper is heated on a glass slide which is set on a heating plate. The temperature of the heating plate is set between 200F to 250F. Once the paper has heated, the catalyst ink is painted onto the carbon. This is done by painting the ink in rows from one side to the other of the paper. The isopropanol and water is allowed to evaporate, and then the next row is painted. Once enough rows are painted to cover the entire GDE the paper is rotated 90 degrees and rows are painted again.

The ink can have a tendency to migrate to the edges of the paper, causing a buildup at the edges. To avoid this issue, the first five layers that are painted on can be

painted in a different method. Instead of painting from one side to the other (i.e.: left to right), the ink can be painted from the center to the edge. When this center-to-edge painting method is employed, the majority of the ink is applied to the center. After a few layers are applied in this way, the rest of the layers can be applied by painting from side to side to achieve an evenly distributed catalyst across the carbon.

Layers of catalyst were painted on until the carbon paper could not be seen through the catalyst layer. Extra layers were painted on after this point in some cases causing a minor increase in the performance due to the presence of additional catalyst. Once the catalyst was painted on, an MEA could be pressed. The catalyst loading was approximately $1\text{mg}/\text{cm}^2$ for the results that are listed.

PRESSING THE MEA AND TESTING:

The GDEs that were painted were used for the anode of an MEA. The cathode was the GDE that was mentioned earlier (from fuelcellstore.com), and the electrolyte was a Nafion 117 membrane. The MEA was pressed for 90 seconds at 275F under 1000lbpf.

This newly prepared MEA was placed in a fuel cell and conditioned for 3-4 consecutive hours a day for 3-4 consecutive days (time varied on an MEA to MEA bases to achieve an optimum level of conditioning) by running the fuel cell with hydrogen as the anode fuel and oxygen as the cathode fuel at 60C. This conditioning process is necessary because some of the catalyst is covered by the Nafion in the ink when the solution is formed, painted, and the MEA is pressed. The pressing of the MEA also causes the pores in the Nafion (in the electrolyte as well as the catalyst layer) to be

reduced in size. The conditioning process helps to open up these pores, as well as create passageways to the catalyst particles^{xxi}.

Once the MEA has reached a point during conditioning where its performance does not increase anymore, it is ready to be tested in a cell with formic acid as the fuel. A simple system was constructed to feed formic acid to a cell. A long PVC pipe was mounted vertically, and a tube was connected to the bottom that ran to the fuel cell. A valve was connected to the tubing, and it was used to control the flow rate. The vertical orientation of the PVC pipe caused the fuel to be gravity fed into the cell. The flow rate could not be controlled as accurately as desired, but this stand provided a simple, low cost method for testing the cell.

The flow rate at the anode must be set low so that the anode is not oversaturated with formic acid. Oxygen was supplied to the cathode at a flow rate of around 50 cc/min (AIR). The cell was heated to 60C. All of the data was obtained using the electronics in the same fuel cell stand which was used with the hydrogen cell.

When the GDE obtained from fuelcellstore.com was used, the performance of the cell decreased rapidly as the cell was run. This is because the catalyst on these GDEs is platinum based, and platinum is quickly poisoned by formic acid. Though formic acid is not being fed to the cathode, it is crossing over the membrane and poisoning the cathode. Not only is it poisoning the cathode, but when the formic acid reacts with the platinum, hydrogen is formed on the cathode, and this waists some of the oxygen at the cathode that is meant to be used to run the fuel cell. Once formic acid begins crossing over, it causes the cathode's performance to decrease in multiple ways.

To fix this, a GDE with Pd/C as the catalyst (just like the anode) was used on the cathode. When the formic acid crosses over to a cathode with a Pd/C catalyst, it will still react with the catalyst and cause some of the oxygen to be wasted, but none of the catalyst should be poisoned.

By using this Pd/C catalyst on the cathode, the performance of the cell increased. After the cell ran for one to two hours, the performance dropped enough due to the formic acid cross-over that the cell was shut off. In contrast to when platinum was used at the cathode, when palladium was used, the cell would perform well the next time it was tested, because the cathode catalyst was not poisoned.

Once acceptable, consistent results were obtained from the formic acid cell over multiple days and iterations of testing, it was assumed that the preparation and conditioning procedure for the GDEs was acceptable. The next step was to test GDEs that were prepared in this fashion in a hybrid cell.

THE HYBRID CELL:

The hybrid cell was designed to replace Nafion with a cheap sponge that would “wick” formic acid into it. This sponge was sandwiched between two plates that were prepared in house (as described earlier) to be used as the housing. A channel was formed in these plates so that the two GDEs, as well as the sponge, would have a place to reside within the housing. The channel ran out the bottom of the cell creating an opening at the bottom, but all other edges were closed.

The sponge used was very thin and relatively dense. A piece of sponge was cut out to be long and narrow. This piece was made to be long enough that it would run out the bottom of the cell housing. When the housing was mounted, the sponge could hang out the bottom and sit inside of a cup containing a formic acid solution. The sponge was then able to wick the acid solution into the cell, and the cell could use the acid as the electrolyte as well as the fuel.

The anode and cathode GDEs were placed on either side of the sponge. It is important that the GDEs have intimate contact with the electrolyte (formic acid in this case), but it is also important that the cathode is not saturated with the formic acid.

Initial tests were performed in the hybrid cell by using cathode and anode GDEs that were prepared in the same fashion as those mentioned above (which were used in the H_2/O_2 cell). Different tests were performed in order to evaluate how changing the molar concentration of the formic acid affected the performance of a cell.

The cell housing was held tightly together by plastic screws. Teflon gaskets were used to keep the anode and cathode electronically separated. Windows were cut into the faces of the housing blocks, which allowed air to reach the back of the anode GDE. Oxygen was supplied to the cathode GDE through the window. This was done so that the CO_2 formed at the anode could escape, and so that pure oxygen could be blown onto the cathode. The hybrid cell was tested using the hydrogen fuel cell stand in the same manner that the formic acid fuel cell had been.

Normally the concentration of formic acid used in a fuel cell ranges from 1M to 10M. It is not advisable to exceed 10M because of cross-over issues in the cell. Since the electrolyte is composed of formic acid in the hybrid cell, cross-over issues are not a

consideration (the nature of the cell means that it is constantly crossing over), so concentrations greater than 10M were observed. An issue with increasing the concentration is that the electrical conductivity of the electrolyte increases, so higher concentrations of formic acid caused the cell to perform poorly.

An OCV of 0.4V was achieved by the hybrid cell. The highest current drawn off of the cell was 15mA. Neither of these results were substantial, (the system was evaluated and a method of improvement was implemented.

In order to reduce the formic acid that was in contact with the cathode GDE, 5wt% Nafion solution was painted onto the cathode GDE to form layers. Though the formic acid will easily cross this thin layer of Nafion, the intent was to have the layer decrease the flux of formic acid from the sponge to the cathode GDE, and in doing so, decrease the amount of formic acid that reacts at the cathode (and waists the oxygen). Except for the extra layer of Nafion, the cathode GDEs were prepared in the very same manner as those described earlier.

IV. RESULTS

A description of the results that were acquired through experimentation is listed below. The data and information detail the major steps followed to find the optimal

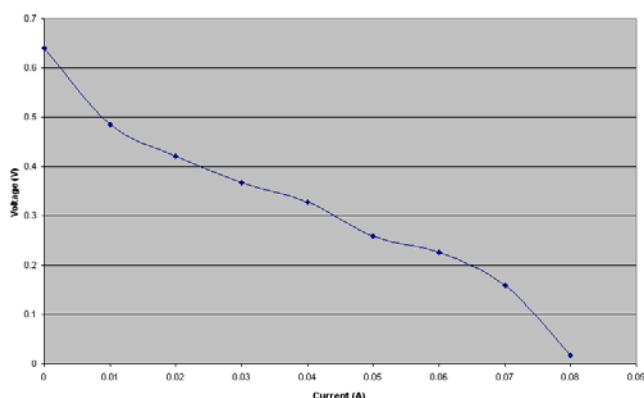


Figure 42: Polarization curve for initial tests of unpressed store bought MEA in FAFC Hardware

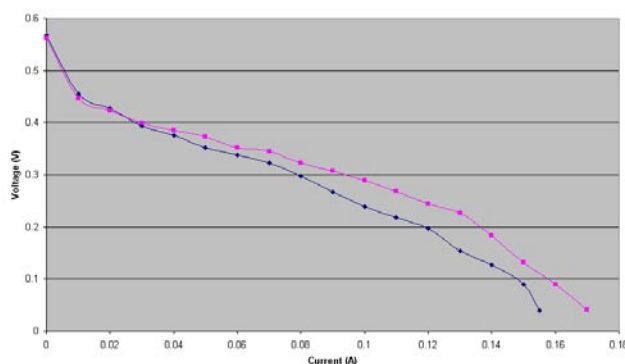


Figure 43: Polarization curve for tests of pressed MEA FAFC Hardware. Pink line is 5M FA and Blue is 3M FA

process for preparing an MEA, as well as designing and testing a hybrid cell. For additional details about the extensive test variables that were considered, see Appendix A.

Initial tests of the fuel cell hardware are shown in Figure 42. The store bought MEA was not conditioned, and the catalyst was platinum based. A more significant issue is that the MEA was not pressed. The unfavorable results are most likely due to a combination of all these factors. From Figure 42, it can be seen

that the maximum current was around 8mA, which is far below the desired results. Later tests were performed on store bought MEAs which were platinum based, and these MEAs were conditioned.

Figure 43 shows the results obtained from a store bought MEA which was pressed. The results are better than those seen in Figure 42, but the maximum current that could be drawn is still very low. Two sets of results are shown here, one for 3M formic acid, and the other for 5M.

Palladium based catalyst were prepared for the anode using the method described earlier. The initial microwave assisted polyol method did not bring about any conclusive results due to poor preparation of the catalyst ink, as well as a lack of conditioning. No current could be drawn off of a FAFC using the catalyst ink prepared in this way. It should once again be noted that the catalyst was not stirred vigorously, so there were large pieces, and the painting method was not well established yet.

Because of the unfavorable results, a new method was approached. The new method was used by the University of Illinois for their FAFC research. The method is a sodium borohydride reduction method for producing Pd/C. The first iteration of catalyst preparation was not stirred as rigorously as it should have been (it was magnetically stirred and sonicated in a bath instead of being sonicated using a rod). Due to the poor preparation procedures, as well as a lack of conditioning, results could not be obtained from the cell.

After multiple catalysts were prepared, it was understood that there was a problem with the preparation procedure. Three different steps in the overall preparation process were

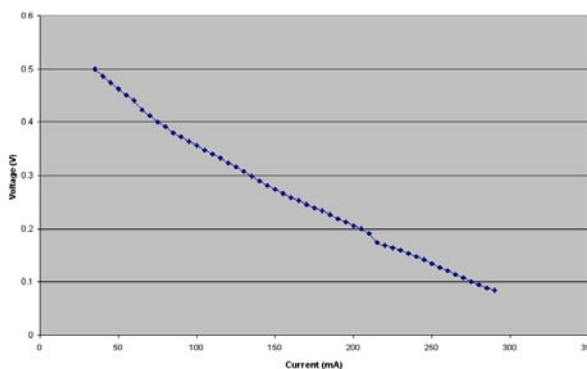


Figure 44: Polarization curve after stirring with sonicator rod.

added.

The first
change to the catalyst
preparation process

was to change the
stirring procedure. It

was decided to use a magnetic stirring rod to prepare the catalyst ink as well as to finely distribute the carbon in the solution used for preparing the Pd/C catalyst. By using the magnetic stirring rod in these two steps of the procedure, an MEA was formed which had the results listed in Figure 44. As can be seen by comparing this figure to the previous figures, the results are improving, but the desired maximum current should be $>1A$, indicating that the optimum design has not been reached.

The next step that was added to the preparation process was a change to the painting method used to apply the catalyst ink to the carbon paper (GDL). Originally, the

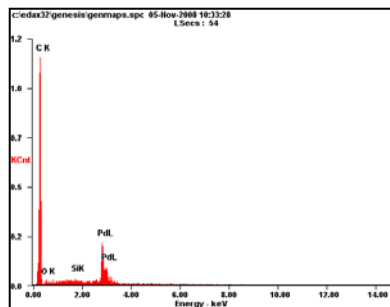


Figure 46: Data collected off portion of Figure 48 with cross-hairs over it

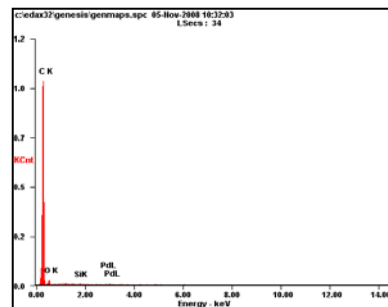


Figure 45: Data collected off dark portion of Figure 48 showing elements present in sample location

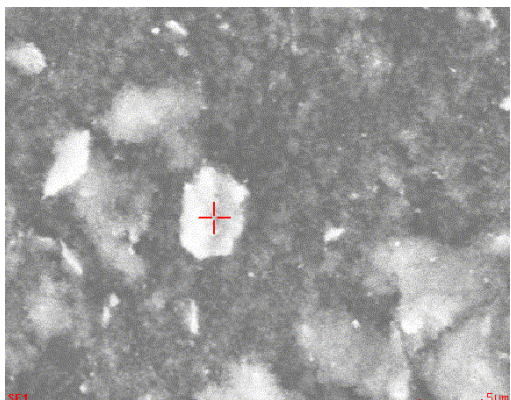


Figure 48: SEM image of a catalyst prepared with a bad stirring method

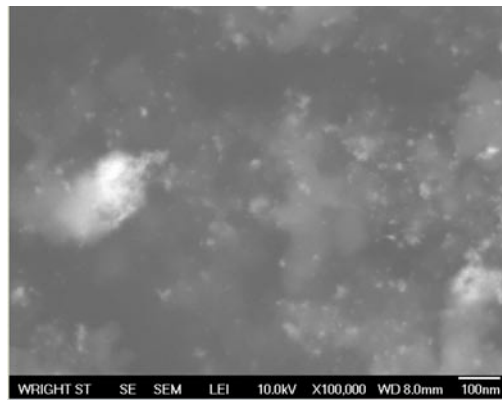


Figure 47: SEM image of catalyst ink once proper preparation procedures are used

ink was painted on at room temperature, and only a single layer was painted, but the low temperature made the painting process difficult. Instead, the catalyst ink was painted at 200F to 250F to help the isopropanol and water in the ink evaporate, and multiple layers

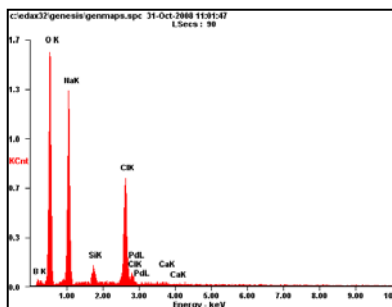


Figure 49: Elements present in NaBH_4 preparation method precipitate

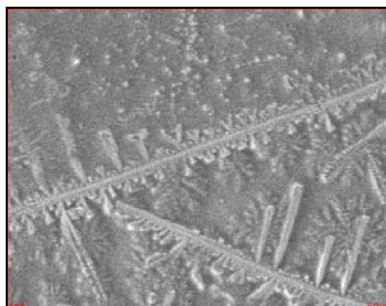


Figure 50: SEM image of precipitate from NaBH_4 catalyst preparation method

were painted onto the GDL to increase the loading of the catalyst.

Along with changing the painting method, the third step was added, which was to

condition the MEA for multiple days inside of the H_2/O_2 fuel cell.

Figure 47 shows an SEM image taken from a catalyst that was prepared with an insufficient stirring method. Figure 45 and Figure 46 show the data obtained from the catalyst when focused on the different areas. When focused on the large white agglomerations (which the cross hairs are on in the image) the reading is given by Figure 46. As can be seen in this data, palladium is present as well as carbon. This is because the focus is on a large Pd agglomeration which is over 0.5 micrometers.

When the focus is on the dark area(focusing on the carbon tape which the Pd/C is spread on), the reading shows that there is no palladium present (Figure 45).

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>BK</i>	30.18	43.37
<i>OK</i>	40.11	38.95
<i>NaK</i>	19.22	12.99
<i>SiK</i>	01.18	00.65
<i>ClK</i>	09.01	03.95
<i>PdL</i>	00.11	00.02
<i>CaK</i>	00.19	00.07
<i>Matrix</i>	Correction	ZAF

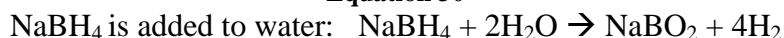
Figure 51: List of elements present in NaBH_4 preparation method precipitate

Figure 48 shows an SEM image of the catalyst ink once proper preparation methods are applied to all processes. Over most of the image, the ink has well distributed Pd particles that are 7nm to 10nm in size.

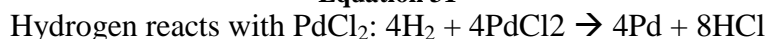
The precipitate of the sodium borohydride procedure was also analyzed. The precipitate was examined to see if any palladium was present. If palladium was present, it would indicate that something was wrong with the preparation procedure and the loading of palladium on the carbon may not be as high as expected . Figure 49 shows an SEM image of the precipitate. The crystal structure is to be expected because salt (NaCl) should be in the precipitate.

The reaction that is expected to take place when the Pd/C is formulated is:

Equation 30



Equation 31

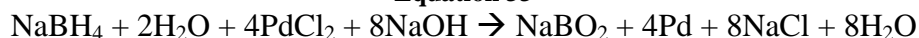


Equation 32



So the overall reaction that takes place when the Pd/C is formulated is meant to be:

Equation 33



As is shown by Figure 50 and Figure 51, the expected precipitate is present, but there is

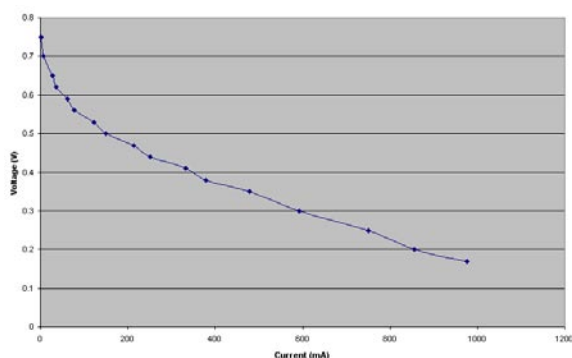


Figure 52: Polarization curve of MEA tested in H_2/O_2 cell. Anode=Pd/C, Cathode=Pt/C

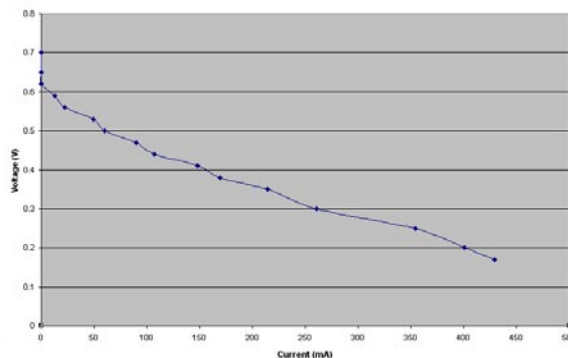


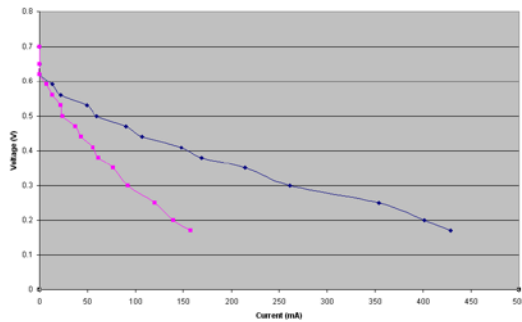
Figure 53: Polarization curve for MEA tested in FAFC. Anode=Pd/C, Cathode=Pt/C

an insignificant amount of palladium in the precipitate. The results for the performance of the MEA in a hydrogen fuel cell are shown in Figure 52, and the performance in the formic acid fuel cell can be seen in Figure 53. As the MEA was tested, its performance degraded. This can be seen for two consecutive tests in Figure 54. The MEA degraded far too quickly to even consider the results as a minor success. Tests were performed on future MEAs which were prepared in the same manner, but quick degradation of performance was always an issue.

With this data, it was apparent that the catalyst was working in the formic acid fuel cell, but it was most likely being poisoned. Since it was already understood that formic acid would poison the cathode catalyst (which was platinum based), Pd/C was used on the cathode as well as the anode.

The cathode GDE was prepared in the same manner as the anode GDE had been. When Pd/C is used on the anode and the cathode, the cell is protected against the poisoning that takes place when platinum is used as a catalyst. Figure 55 and Figure 56 show the results of using Pd/C at the cathode and the anode for a hydrogen cell and a formic acid cell respectively.

When an MEA made with Pd/C on the anode and the cathode was used in an H_2/O_2 cell, the cell reached currents greater than 4 amps at 0.17V after being conditioned



for 5-10 hours. When the same MEA was used in a formic acid cell, the current reached at 0.17V was greater than 2 amps.

Three MEAs were prepared in the

Figure 54: Consecutive test results for MEA tested in FAFC. Anode=Pd/C, Cathode=Pt/C

the anode and the cathode), and each performed as well as those shown in Figures 55 and 56. With adequate results consistently obtained from the Pd/C GDEs prepared in-house, the hybrid cell could now be tested with the Pd/C GDEs that were prepared using

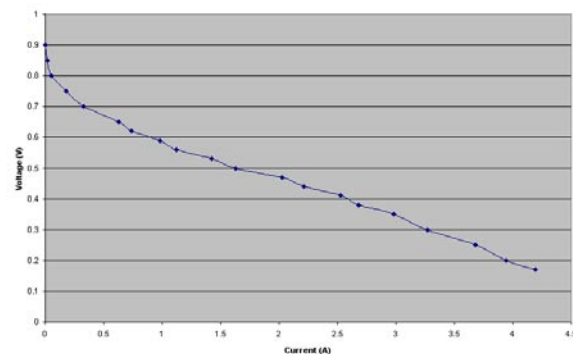


Figure 55: Polarization curve for MEA tested in a H_2/O_2 cell. Anode=Pd/C, Cathode=Pd/C

preparation process established. The GDEs that were used in the H_2/O_2 and formic acid cells could not be used in the hybrid cell because they had been pressed to the Nafion. When the GDEs were peeled off of the Nafion after conditioning, a majority

of the catalyst remained on the Nafion.

GDEs for the hybrid cell were prepared by painting Pd/C catalyst ink onto the cathode and anode GDL. Instead of pressing the GDEs to form the MEA, the electrolyte membrane and GDEs were placed into the cell unpressed. The cell was run for 10 hours to condition the GDEs. Once the conditioning was done, the GDEs were placed into the hybrid formic acid cell. Since the GDEs were unpressed, the catalyst was not removed from the GDE when the MEA was disassembled.

Many tests were performed on the hybrid cell using the conditioned GDEs. A stable OCV of around 400mV was obtained from the cell. The maximum current that could be drawn off of the cell was 17mA.

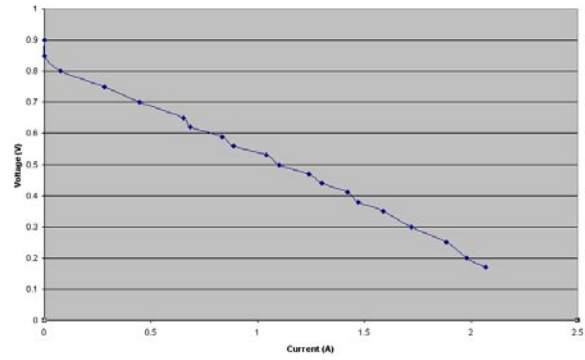


Figure 56: Polarization curve for MEA tested in a FAFC. Anode=Pd/C, Cathode=Pd/C

V. CONCLUSION

Testing of the hybrid formic acid fuel cell showed that it was not capable of producing significant current. This could be due to formic acid at the cathode, CO_2 at the anode, ohmic resistance because of the windows which were cut into the cell housing, and issues with electrical conductivity across the formic acid membrane.

With the current configuration, even if Nafion solution is painted onto the cathode GDE, formic acid will still reach the cathode catalyst. Having formic acid present will not cause the catalyst to be poisoned, but it will cause hydrogen ions to be formed at the cathode. The oxygen can react with the hydrogen and form water. This is the reaction that should take place on opposite sides of the cell. When both take place at the cathode, the oxygen, which is to be used with the hydrogen ions formed at the anode, is wasted.

At the anode, when the formic acid (HCOOH) reacts with the catalyst, 2H^+ , 2e^- , and CO_2 are formed. Since there is no flow of formic acid through the cell, the CO_2 has no means of being drawn away from the catalyst. This could lead to a buildup of CO_2 at the anode catalyst.

Windows are cut in the conductive housing of the cell where the anode and cathode GDEs make contact with the housing. The contact between the GDEs and the housing creates a passageway for the electrons to escape to an external circuit. The windows are cut to allow exhaust to escape the cell and to allow oxygen into the cathode,

but by cutting the windows, a majority of the contact between the GDEs and the housing is removed. This causes ohmic resistance which can damage the performance of the cell.

Lastly, while formic acid functions as an ion conducting membrane, it is also electrically conductive. Low concentrations of formic acid must be used to reduce the electrical conductivity of the membrane. Even with low concentrations, the conductivity is still a significant issue.

The CO₂ at the anode, formic acid at the cathode, ohmic resistance caused by the windows in the housing, and electrical conductivity across the membrane all contribute to make the cell run in a sluggish manner. If a system could be formed which causes the formic acid to continually wick through the cell (as it is, the formic acid wicks into the cell, and sits in the sponge once the sponge is saturated), perhaps the CO₂ issue could be resolved. If the cell housing could be formed perfectly around the cathode GDE, and a significant amount of Nafion was painted onto the GDE, the issue of formic acid flooding the cathode could be reduced, but it is unlikely that the issue could be fixed altogether. If the housing could be made porous where the windows were cut, instead of cutting that portion of the housing away entirely, the ohmic resistance could be reduced significantly.

In conclusion, the current configuration of the hybrid formic acid fuel cell is not able to achieve currents significant enough to be useful in electronic applications. There are several options for improvement on the fuel cell design that could increase performance, but these were beyond the scope of this paper and need further investigation.

VI. APPENDIX A

List of Variables and Variable Categories Considered:

When optimizing the preparation and testing of an MEA, many different variables were considered. These variables can be separated into different categories, which are listed below:

Concentration of Formic Acid:

3M

5M

7M

10M

Gasket Configuration:

0.006" Thick

0.010" Thick

Large Active Area Window

Small Active Area Window

Catalyst Preparation:

Hydrophilic or Hydrophobic Carbon

Microwave Assisted Polyol Process

NaBH₄ Process

20wt% PdCl₂

40wt% PdCl₂

Catalyst Ink Preparation:

Stir Ink with Magnetic Stir and Sonication Bath

Stir Ink with Sonicator Rod

With or without TBA in the Ink

With or without Isopropanol in the Ink

Amount of Water in the Ink

Amount of 5wt% Nafion Solution in Ink

With or without Teflon in the Ink

GDL:

Carbon cloth or carbon paper

Painting at high temperature or room temperature

Paint single layer or multiple layers onto GDE

Paint Ink onto GDL, membrane, or both

Testing Temperature:

30C

60C

80C

Fuel Cell Configuration:

Using Store Bought MEA (PtRu/C anode, Pt/C Cathode)

Using Store Bought Cathode and In-House Pd/C Anode for MEA

Using PdCo/C Cathode and Pd/C Anode for MEA

Using Pd/C on Anode and Cathode for MEA

Test using power supply or fuel cell stand

Low fuel flow or high fuel flow

Description of Variables and Variable Categories:

Concentration of Formic Acid:

Formic acid concentration is considered because it determines the amount of hydrogen that will be available to the cell. The performance of the catalyst at the anode has a significantly larger affect than the molar concentration of the fuel, but the concentration is still a factor that needs to be considered.

When direct methanol fuel cells are considered, the molar concentration is relatively fixed due to the cross-over issues associated with methanol. Usually, no

concentration greater than 1M is considered. When Formic Acid is used, higher molar concentrations can be considered because cross-over is not usually as great of an issue.

To formulate the different concentrations of formic acid, highly concentrated formic acid (88wt%, GFS Chemicals) was mixed with the appropriate amount of distilled water to make the desired concentration of formic acid. This solution was added to the reservoir and allowed into the anode of the fuel cell.

Gasket Configuration:

A gasket is placed in the fuel cell on both the anode and the cathode. The gasket is used because the GDEs are in contact with both the ionic membrane and a bi-polar plate. The GDE has a much smaller cross-section than the ionic membrane or the bi-polar plate, so the gasket is used to seal the remainder of the area to keep the fuel cell from leaking.

The necessary thickness of the gasket is determined by the difference between the thickness of the membrane and the sum of the thicknesses of the two GDEs and the membrane (meaning, the difference between the thickness of the active area of the MEA, and the thickness of the Nafion membrane).

The active area window of the gasket is the portion of the gasket that is removed to allow the GDE to cross the gasket from the ionic membrane to the bi-polar plate. A large window will allow excess fuel to pool up around the GDE on the anode side and water to pool up on the cathode side. When testing the same MEA with a large window and a small window gasket in two consecutive tests, the use of a small window gasket increased performance. This is because the pooling of the fuel and water was not

allowing the CO₂ to escape the anode and the oxygen to reach the cathode as easily. It can also cause the catalyst to be removed from the GDE and washed out of the cell.

Catalyst Preparation:

Two different processes were used to prepare Pd/C. While each preparation method proves to formulate Pd/C, the NaBH₄ method was the only one that could create a catalyst that could draw an acceptable current.

The first step of the catalyst preparation is to make the carbon (which the catalyst is supported on) hydrophilic. When the carbon is bought (Cabot XC-72R), it is hydrophobic. This is not desirable since the goal is to have the fuel (which contains the hydrogen that is used to run the cell) contact the catalyst and its support. In early stages of the project, the carbon was not made hydrophilic because it was assumed that the carbon was ready to be used when it was received.

The first process that was used to prepare the catalyst was a microwave assisted polyol process. This process uses ethylene glycol to uniformly heat the solution used to prepare the Pd/C. While this process did yield Pd/C, the catalyst never gave acceptable results.

The microwave assisted polyol process is as follows. The first step in the process is to add 40mg of carbon (hydrophilic) to a solution of 27.8 grams of Ethylene Glycol (for uniformly heating the solution), 1.06grams of PdCl₂ (to provide the Pd as catalyst to be supported on Carbon), and 0.75mL of a solution of KOH and distilled water (solution is formed by mixing 0.25grams of KOH and 24.7grams of H₂O) in a 100ml beaker. This solution is heated in a household microwave for 50 seconds (2450 MHz, 700W). The

goal is to break the bond between the Pd and Cl, and the Pd will adsorb to the surface of the Carbon, while the Cl will form Cl_2 in the solution. The resulting solution is filtered, washed, and heated overnight.

The other process that was used is a sodium borohydride (NaBH_4) reduction process. In this process, NaBH_4 is added to a solution of PdCl_2 , carbon (Cabot XC-72R), and water. The NaBH_4 reacts with the water to form NaBO_2 . The hydrogen that is released from the water and the NaBH_4 reacts with the PdCl_2 to form HCl , and the Palladium adsorbs to the surface of the carbon to form Pd/C.

The weight percent of the catalyst is important because it signifies how much catalyst will be present with a certain weight of Pd/C. Depending on the particle size of the Pd, a smaller weight percent can be used. If the particle size is small enough (7-10nm), 20wt% Pd/C should work well. Because of the difficulties encountered in finding the optimum process for preparing an MEA, 40wt% Pd/C was used for most catalysts.

Catalyst Ink Preparation:

The catalyst ink preparation seems to be one of the most overlooked steps in the preparation of an MEA. Most research papers list the preparation method for a catalyst, and the testing procedure for the MEA, but completely skip over the ink preparation. After many failed attempts, it was understood that one of the largest issues with the early procedures used to prepare an MEA was the catalyst ink preparation.

Isopropanol, water, Nafion, and the catalyst (Pd/C) were the main components added to the ink. These were added in different proportions to find which ratio was the best for creating an ink that was both paintable, and that yielded acceptable results. When

an ink is not paintable, it will either conglomerate at the surface of the GDL, or it will pass through the GDL and end up on the surface of what the GDL is mounted to in the painting process.

From testing different mixtures, it was found that using too much water caused the ink to pool up on the surface of the GDL. Some of the mixtures that were tested are listed below (all weights are in mg), and comments are added to show how the mixtures worked when they were painted:

Isopropanol/H₂O/Nafion

750/750/150 – Quickly passes through the GDL

750/750/500 – Passes through the GDL less, but requires a lot of Nafion

375/1125/500 – Performs the same as 750/750/500

750/350/150 – Paints very well and requires much less Nafion

The mixture that was used in the final configuration was 750/350/100, and it was very paintable without requiring an excessive amount of Nafion.

The amount of Nafion used is very important to consider because Nafion is expensive, and using too much or too little can cause the MEA to have a difficult time functioning. The Nafion in the ink is used to help the ions travel to and from the membrane (depending on if the cathode or the anode is being considered). Too much Nafion would not only waste money, but it could also make it more difficult for the fuel to reach the catalyst in the ink (and extend the necessary conditioning time). Too little Nafion will make it difficult for the ions to find a passageway across the MEA. While the

amount of Nafion was varied in other tests, once the optimal mixture of Isopropanol and water was found, the amount of Nafion was reduced. Tests were performed with no Nafion, 65mg of Nafion, and 100mg of Nafion.

Two variations of the ink preparation that caused little or no improvement to the end result were adding Teflon and/or TBAOH (Tetrabutylammonium Hydroxide). When these were added, the performance of the MEA either dropped, or had no obvious change. TBAOH was added to try to help the paintability of the ink. Adding the TBAOH did not have a significant impact, and by changing the ratio of water, Isopropanol, and Nafion, the ink became paintable without adding any new ingredient to the ink.

Teflon is added to keep the catalyst layer from flooding. It is commonly used at the cathode since water can build up and suffocate the cathode. When Teflon was added, the MEA did not perform any better, and it tended to perform much worse, so Teflon was not included in the final preparation process.

The final part of the ink preparation process is the stirring of the ink. The ink is prepared in a 10mL beaker. The ink must then be stirred to obtain a well distributed ink and, more importantly, to break up the large particles of Pd/C. When the Pd/C is added to the ink, it is in large chunks. Though the chunks are broken down in any stirring procedure, they must be broken down to very fine particles so that they can mix into the ink. The end result should be a dark, homogenous ink rather than a clear heterogeneous ink with visible particles. If the ink is heterogeneous, then the ink will not function well, and could risk not functioning at all.

Early ink preparation involved stirring the catalyst with a magnetic stirring rod. There were many problems with this procedure. First of all, the proper proportion of

water, Isopropanol, and Nafion had not been discovered (and in very early versions, Isopropanol was not used at all). The other issue was that the stirring rod did not do an acceptable job of breaking the Pd/C into a fine powder that could be distributed through the ink. Instead, the ink was a thick, clear liquid which consisted of the Nafion and water (because most of the water and all of the Isopropanol had evaporated) with large chunks of Pd/C in it. This was painted onto the surface of the GDL. The GDE ended up having an uneven surface because of the large particles of Pd/C. When the GDE was prepared this way, it was never possible to obtain a significant current from the MEA.

Later ink preparation methods involved using a sonicator rod. The beaker was mounted and the rod was submerged in the ink. The sonicator was run for 3 minutes, and after this time the ink was very paintable (if the correct mixture of water, Isopropanol, and Nafion was used), and the Pd/C particles were fine and mixed into the ink. There were still a few large particles visible at the bottom of the beaker once the ink was painted on, but this was not significant unless these particles were applied to the GDL by accident (if the particle stuck to the paint brush when the ink was being applied).

GDL:

After the catalyst ink is prepared it must be applied to a GDL (gas diffusion layer). Once the catalyst ink is applied, the GDL is known as a GDE (gas diffusion electrode). There are multiple ways of applying the catalyst ink, but the one used in this case was a painting method. Once the catalyst ink was prepared, a thin hobby paint brush was used to apply the ink in rows along the length of the GDL. After enough adjacent

rows had been painted to cover the entire GDE, the GDE was turned 90 degrees and rows were painted again to form multiple layers of catalyst.

One of the choices that must be made is whether to use carbon cloth or carbon paper for the GDE/GDL. Carbon cloth is flexible and does not fall apart as easily, so it is easier to work with (there are many points in the MEA preparation and testing process in which it is easy to break the GDE). Because of this, earlier testing used carbon cloth.

In later tests, carbon paper was used. Carbon paper is very stiff and easy to break, but it is also easier to paint onto. While the ink seems to have an easier time passing through the carbon cloth, it paints well onto the surface of the carbon paper. Once a few layers have been painted on, the painter can see the layer forming on the surface. The fuel cells tested with carbon paper also tended to give significantly better results.

The painting temperature is very important for preparing the GDE. In the early phases of the project, the ink was painted on at room temperature. The problem with this is that the water and Isopropanol do not evaporate quickly enough, so as layers are painted, the surface becomes saturated, and the entire process is either slowed down immensely or ruined because of the excess liquid.

If the ink is painted on while the GDL/GDE is being held at a higher temperature, then as the rows are painted on, the excess liquid evaporates in a matter of seconds and another row can be painted adjacent to the previous row with no fear of the liquid pooling. It is important not to use a temperature that is too high because of the Nafion that is present. If the temperature is too high, the Nafion can degrade, which will damage the performance of the GDE.

In early tests (when using a magnetic stirrer instead of the sonicating rod), only a single layer of catalyst ink was painted onto the surface of the GDL. This was mainly because there was not much ink obtained from the stirring method, but also because the surface was covered in large chunks of catalyst. Once a proper painting method was used, multiple layers were painted on the GDL to form a GDE that performed well.

One last consideration was where the ink should be painted. Some resources preferred to paint the catalyst ink directly onto the ion exchanging membrane. This ensures that the catalyst layer has intimate contact with the membrane. When this method was applied, the membrane would almost immediately deform because of the liquid that was in contact with one side of the membrane. It was later understood that other equipment was necessary to perform this type of catalyst application. Because the proper equipment was not available, the catalyst ink was only applied to the GDL/GDE. This method did not inhibit the testing because applying catalyst ink only to the GDL/GDE is a common method as well. The membrane application method was only tested to ensure that it would not yield better results.

Testing Temperature:

The testing temperature of the fuel cell is important because as the temperature rises, more energy is available to assist the catalyst kinetics. The three main temperatures that data was recorded at are 30C, 60C, and 80C. The data was recorded at 30C to obtain room temperature data from the cell. The 60C testing was recorded because it is a common temperature tested in this area of fuel cell research, so this data could be compared to results found in other papers. The 80C data was recorded because the MEA

was run at this temperature for long periods of time during the conditioning procedure. By recording the 80C data, the results of conditioning could be observed.

Fuel Cell Configuration:

Multiple configurations were used in the process of finding the optimal anode and cathode catalyst, as well as the best equipment to test with. To begin with, store bought MEAs were used. These MEAs had PtRu/C as the anode catalyst, and either PtRu/C or Pt/C as the cathode catalyst. The MEA was not conditioned at this early point in the project. The MEAs were tested in the FAFC but performed poorly. Later in the project, an MEA was purchased and conditioned. The polarization curve of the MEA when tested with hydrogen was excellent, but the MEA performed terribly in the FAFC. This was most likely due to the anode and cathode catalysts which were poisoned by the formic acid.

The next step was to prepare an anode catalyst in-house, and use a store bought Pt/C catalyst at the cathode. While this helped in formulating a method for preparing Pd/C catalysts, the tests never yielded good results because of the poisoning of the Pt/C at the cathode.

It was understood that poisoning was an issue, so PdCo/C was used at the cathode. PdCo/C is a catalyst that has been found to be tolerant to methanol, so the intent was that it would also be tolerant to formic acid. The results from the catalyst were minimal, so PdCo/C was not considered as a viable option for a cathode catalyst. The minimal results could be due to the fact that the new process was not experimented with

enough because of a lack of time, or that the PdCo/C is not tolerant to formic acid.

Further testing could achieve different results.

The final configuration was to have Pd/C at the anode and the cathode. This configuration worked well because the cross-over formic acid did not poison the catalyst. This was the configuration that yielded results that far surpassed anything that was previously obtained for the project.

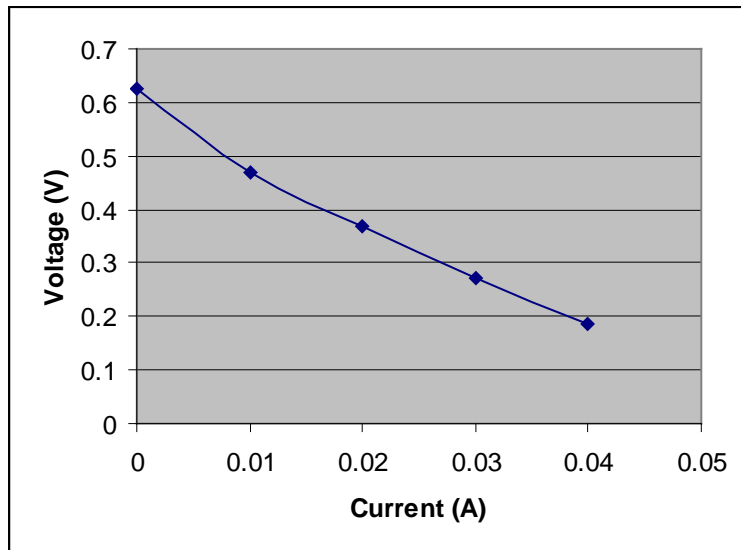
One other configuration consideration was what testing equipment to use. Initially, a power supply was used to obtain all of the readings from the cell. Later in the project, a fuel cell stand was used. By comparing the results from each, it could be seen that the power supply gave inferior results. The data appeared to be inaccurate, because as the cell was being heated, the current reading would increase, and when the heater shut off, the current would decrease. This shows that there was some electrical interference from the heater and the power supply was reading it and not accounting for it, but rather reading it as if the fuel cell was providing the extra power.

The fuel flow will determine what amount of hydrogen will be available to the cell (from the formic acid, HCOOH), but that does not mean that having excessive amounts of fuel will increase cell performance. When the fuel flow is slightly increased, it will cause the results to decline due to cross-over issues as well as issues with pooling of formic acid at the anode (oversaturation). The best results were obtained by having the very lowest fuel flow possible with the equipment that was used.

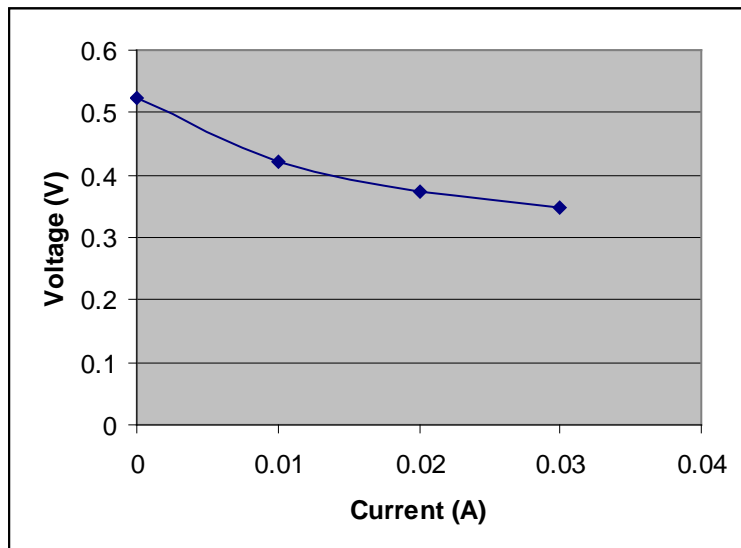
Experimentation with Different Variables: (Variables that change from previous test are in bold)

A small number of the tests that were performed are listed below along with the variables that were used.

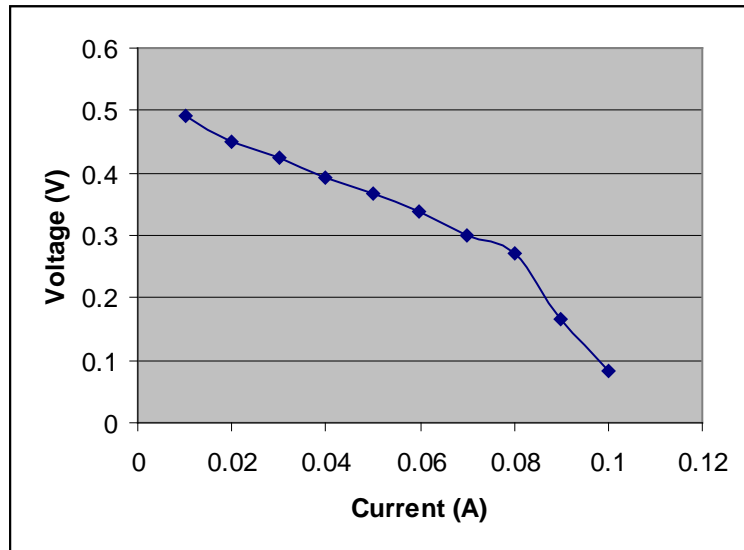
MEA: Store Bought
Cell Type: Formic Acid
Fuel Cell
Fuel Concentration: 3M
Testing Temperature:
30C
Conditioned?: No
Fuel Flow: High
Gasket: Large Window



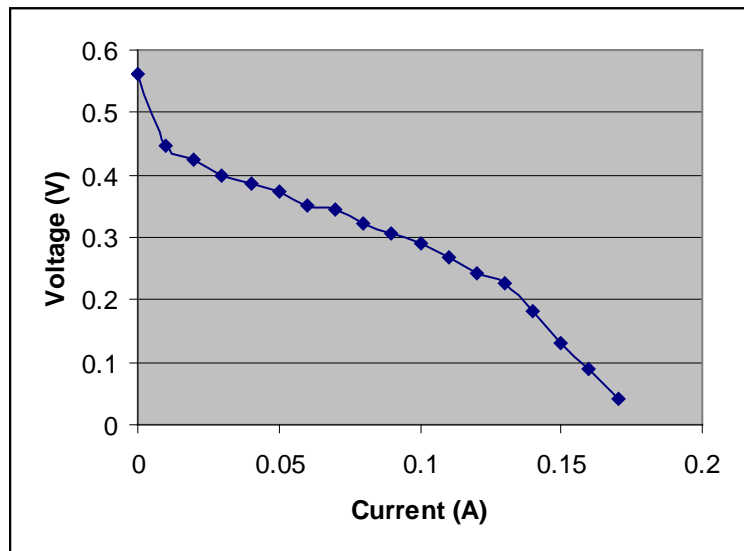
MEA: Store Bought
Cell Type: Formic Acid
Fuel Cell
Fuel Concentration: 5M
Testing Temperature:
30C
Conditioned?: No
Fuel Flow: High
Gasket: Large Window



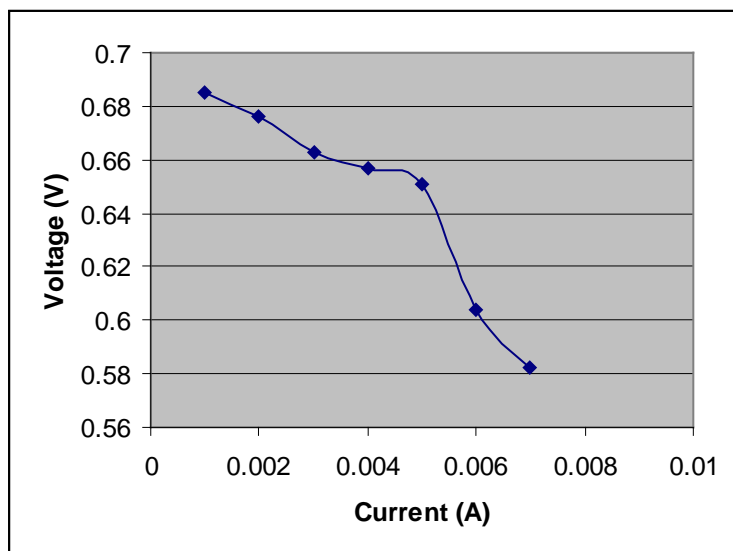
MEA: Store Bought
Cell Type: Formic Acid
Fuel Cell
Fuel Concentration: 3M
Testing Temperature: 30C
Conditioned?: No
Fuel Flow: Low
Gasket: Large Window



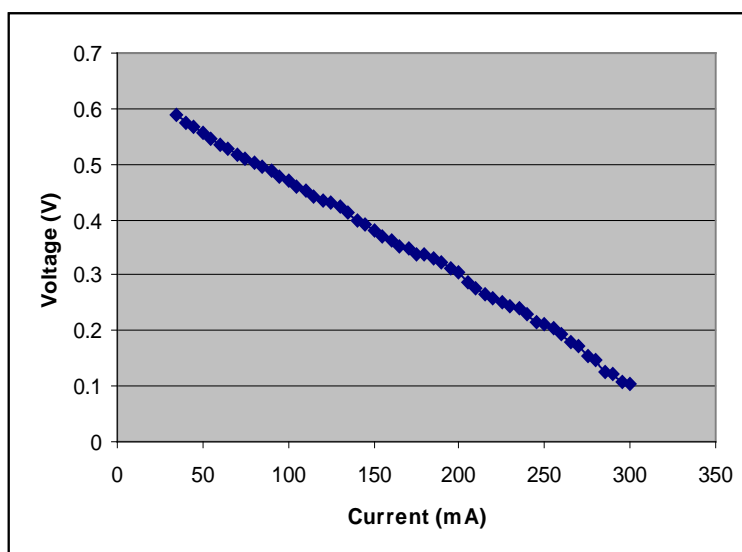
MEA: Store Bought
Cell Type: Formic Acid
Fuel Cell
Fuel Concentration: 5M
Testing Temperature: 30C
Conditioned?: No
Fuel Flow: Low
Gasket: Large Window



MEA: Store Bought
Cathode,
Pd/C Anode (NaBH₄, 40wt%)
Ink Preparation: Magnetic Stirrer
Carbon: Hydrophilic
Cell Type: Formic Acid Fuel Cell
Fuel Concentration: 5M
Testing Temperature: 30C
Conditioned?: No
Fuel Flow: Low
Gasket: Large Window
Paint Method: Cloth



MEA: Store Bought
Cathode,
Pd/C Anode (NaBH₄, 40wt%)
Ink Preparation: Magnetic Stirrer
No Nafion/TBA, add isopropanol
Carbon: Hydrophilic
Cell Type: Formic Acid Fuel Cell
Fuel Concentration: 5M
Testing Temperature: 80C
Conditioned?: No
Fuel Flow: Low
Gasket: Large Window
Paint Method: Cloth



MEA: Store Bought

Cathode,

Pd/C Anode (NaBH₄,
40wt%)

Ink Preparation: Magnetic
Stirrer

10mg Nafion, add
isopropanol

Carbon: Hydrophilic

Cell Type: Formic Acid

Fuel Cell

Fuel Concentration: 5M

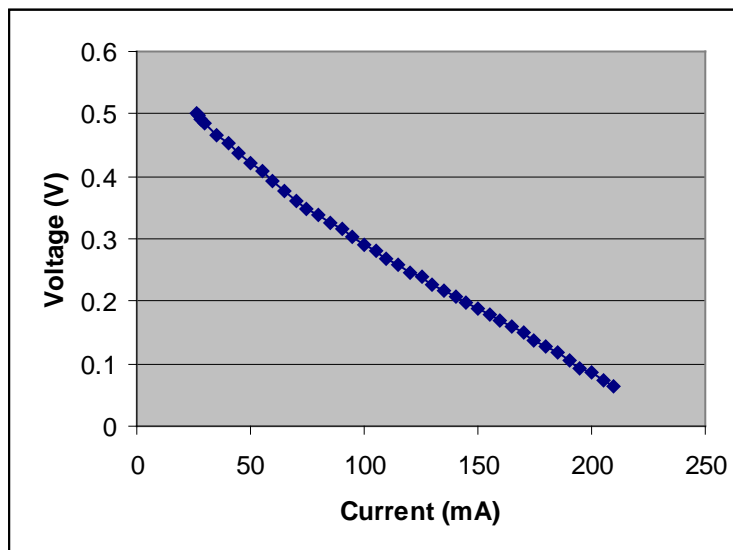
Testing Temperature: 80C

Conditioned?: No

Fuel Flow: Low

Gasket: Large Window

Paint Method: Cloth



MEA: Store Bought

Cathode,

Pd/C Anode (NaBH₄,
40wt%)

Ink Preparation: Magnetic
Stirrer

65mg Nafion, add
isopropanol

Carbon: Hydrophilic

Cell Type: Formic Acid

Fuel Cell

Fuel Concentration: 5M

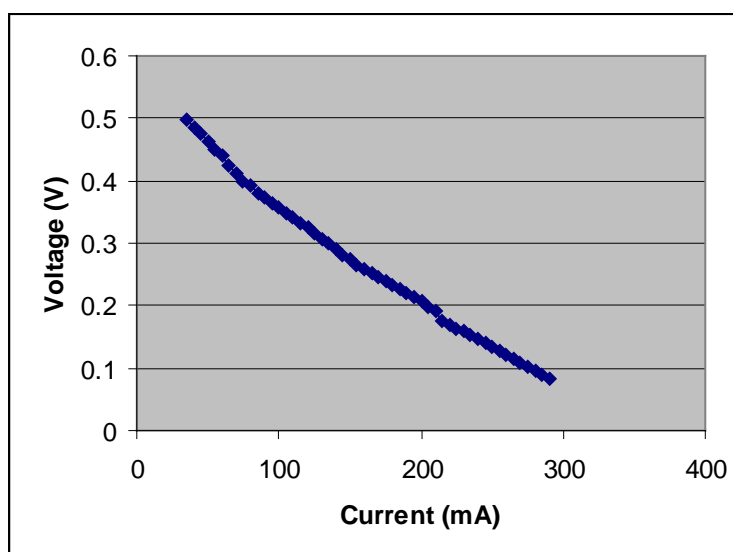
Testing Temperature: 80C

Conditioned?: No

Fuel Flow: Low

Gasket: Large Window

Paint Method: Cloth



MEA: Store Bought

Cathode,

*Pd/C Anode (NaBH₄,
40wt%)*

Ink Preparation: *Magnetic
Stirrer*

65mg Nafion, *add
isopropanol*

Carbon: Hydrophilic

Cell Type: Formic Acid

Fuel Cell

Fuel Concentration: 5M

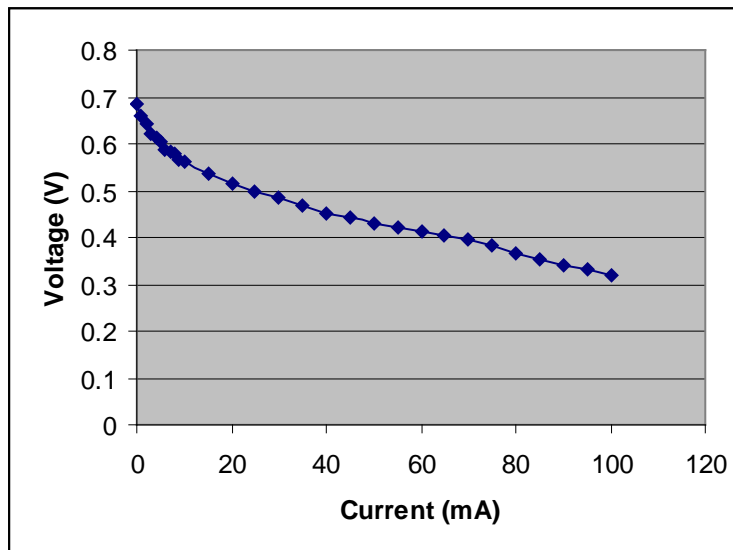
Testing Temperature: 80C

Conditioned?: No

Fuel Flow: Low

Gasket: Large Window

Paint Method: Cloth and Membrane



MEA: Pd/C painted onto

store-bought Pt/C for

Cathode,

*Pd/C Anode (NaBH₄,
40wt%)*

Ink Preparation: *Magnetic
Stirrer*

100mg Nafion, *add
isopropanol*

Carbon: Hydrophilic

Cell Type: Formic Acid

Fuel Cell

Fuel Concentration: 5M

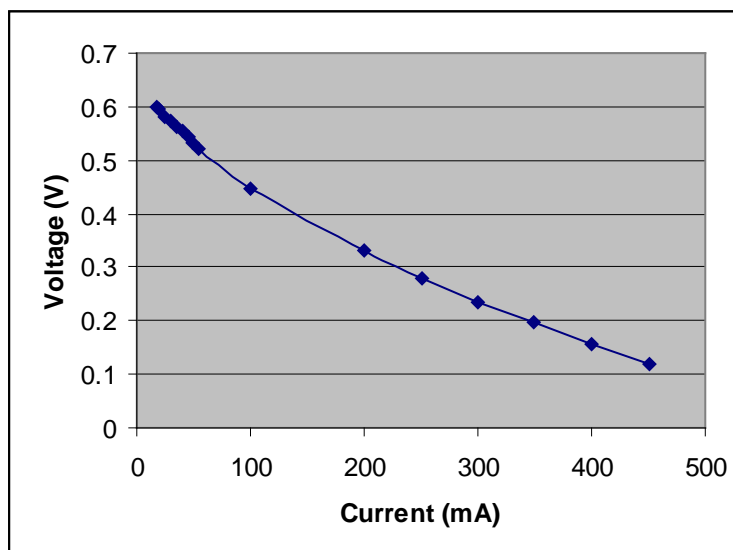
Testing Temperature: 80C

Conditioned?: No

Fuel Flow: Low

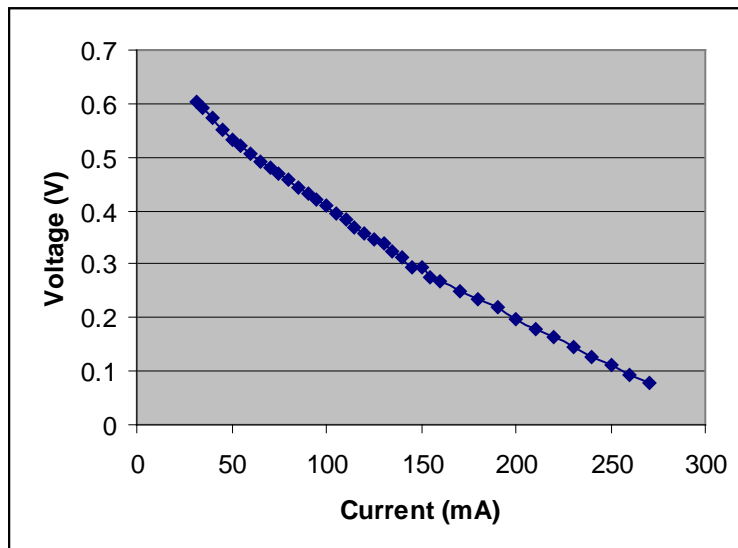
Gasket: Large Window

Paint Method: Cloth

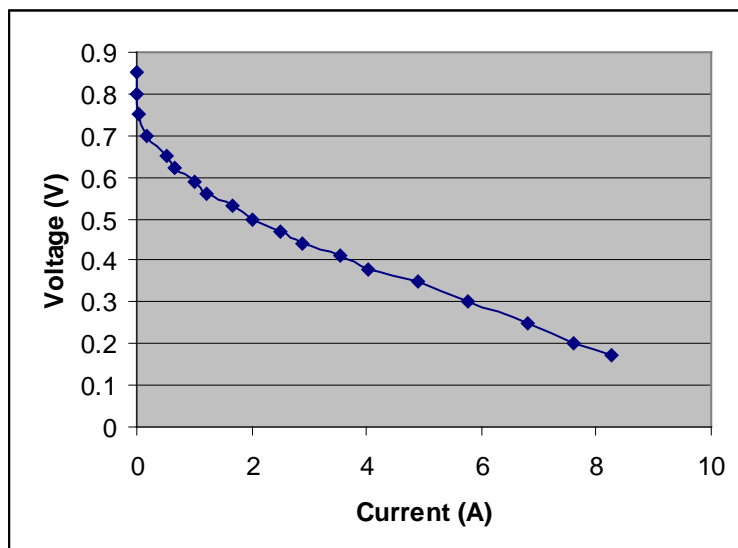


**MEA: PdCo/C Cathode,
Pd/C for Anode (NaBH_4 ,
40wt%),
Quit using PVA in prep.
process**

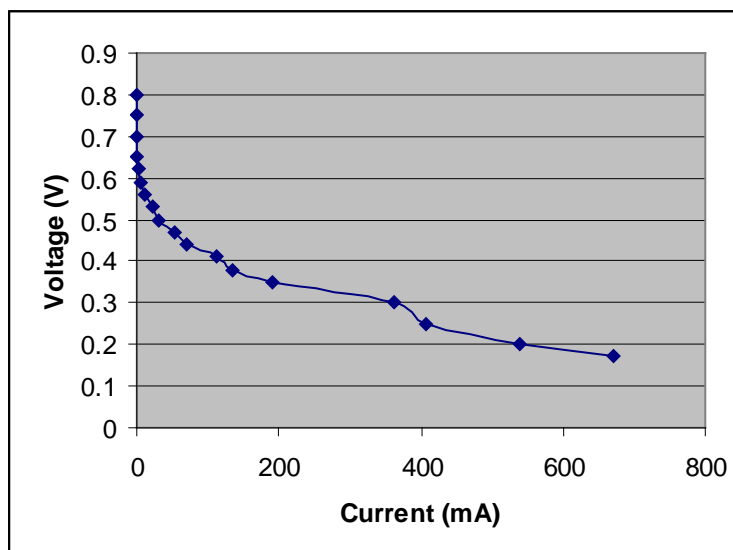
*Ink Preparation:
Magnetic Stirrer
100mg Nafion, add
isopropanol
Carbon: Hydrophilic
Cell Type: Formic Acid
Fuel Cell
Fuel Concentration: 5M
Testing Temperature:
80C
Conditioned?: No
Fuel Flow: Low
Gasket: Large Window
Paint Method: Cloth*



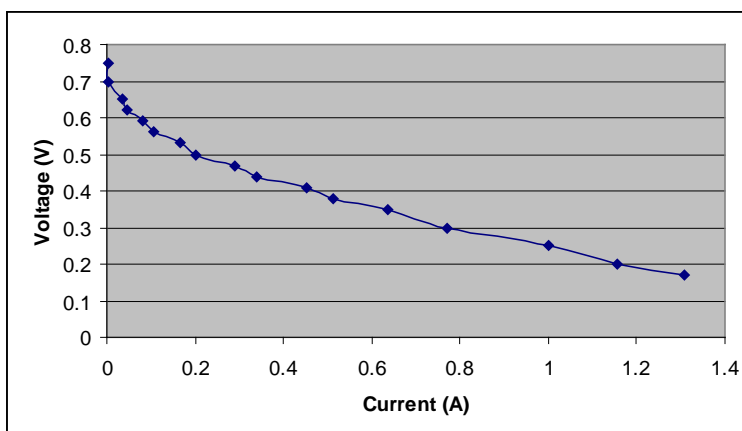
**MEA: Store Bought MEA
Cell Type: H_2/O_2 Cell
Testing Temperature:
60C
Conditioned?: Yes
Gasket: Small Window**



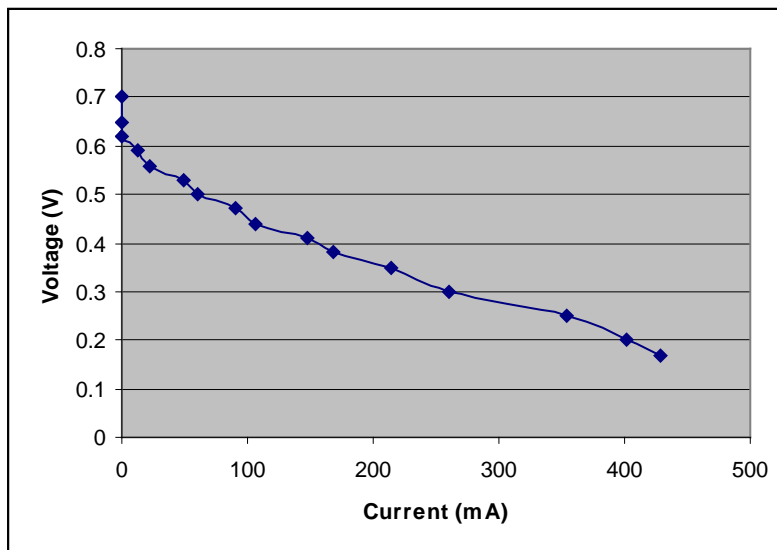
MEA: Pt/C Cathode,
Pd/C for Anode (NaBH₄,
40wt%)
Ink Preparation: Magnetic
Stirrer
 100mg Nafion, add
 isopropanol
 Carbon: Hydrophilic
 Cell Type: H₂/O₂
 Testing Temperature: 60C
 Conditioned?: No
 Gasket: Small Window
Paint Method: Paper,
Using Heating Plate



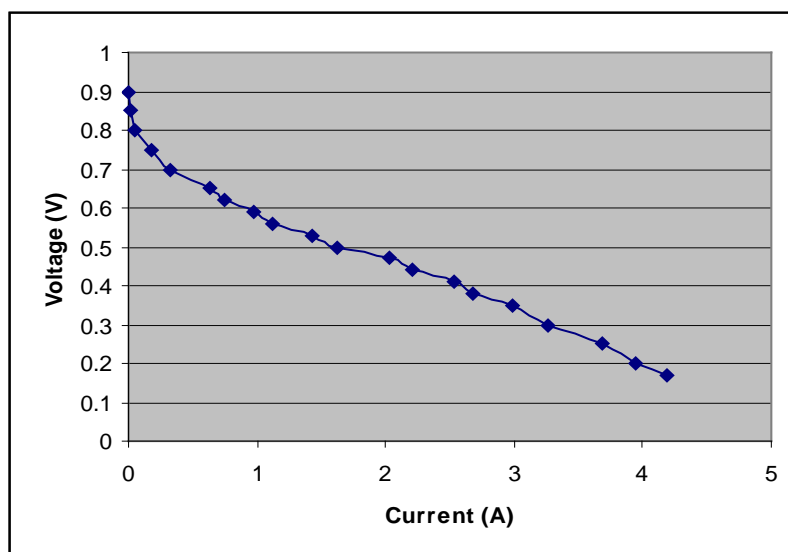
MEA: Pt/C Cathode,
Pd/C for Anode (NaBH₄,
40wt%)
Ink Preparation:
Sonicating Rod
 100mg Nafion, add
 isopropanol,
Too much water in ink
 Carbon: Hydrophilic
 Cell Type: H₂/O₂
 Testing Temperature: 60C
 Conditioned?: No
 Gasket: Small Window
 Paint Method: Paper,
 Using
 Heating Plate



MEA: Pt/C Cathode,
Pd/C for Anode
(NaBH_4 , 40wt%)
Ink Preparation:
Sonicating Rod
100mg Nafion, add
isopropanol,
Carbon: Hydrophilic
**Cell Type: FAFC with
Stand**
Testing Temperature:
60C
Conditioned?: No
Gasket: Small Window
Paint Method: Paper,
Using Heating Plate



MEA: Pd/C Cathode
and Anode
(NaBH_4 , 40wt%)
Ink Preparation:
Sonicating Rod
100mg Nafion, add
isopropanol,
Carbon: Hydrophilic
Cell Type: H_2/O_2
Testing Temperature:
60C
Conditioned?: Yes
Gasket: Small
Window
Paint Method: Paper,
Using Heating Plate



MEA: Pd/C Cathode
and Anode

(NaBH_4 , 40wt%)

Ink Preparation:

Sonicating Rod

100mg Nafion, add

isopropanol,

Carbon: Hydrophilic

Cell Type: FAFC

with stand

Testing Temperature:

60C

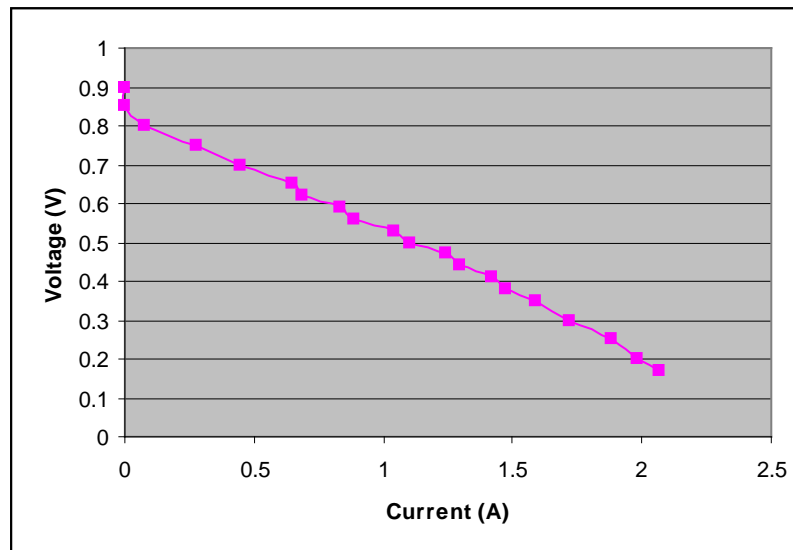
Conditioned?: Yes

Gasket: Small

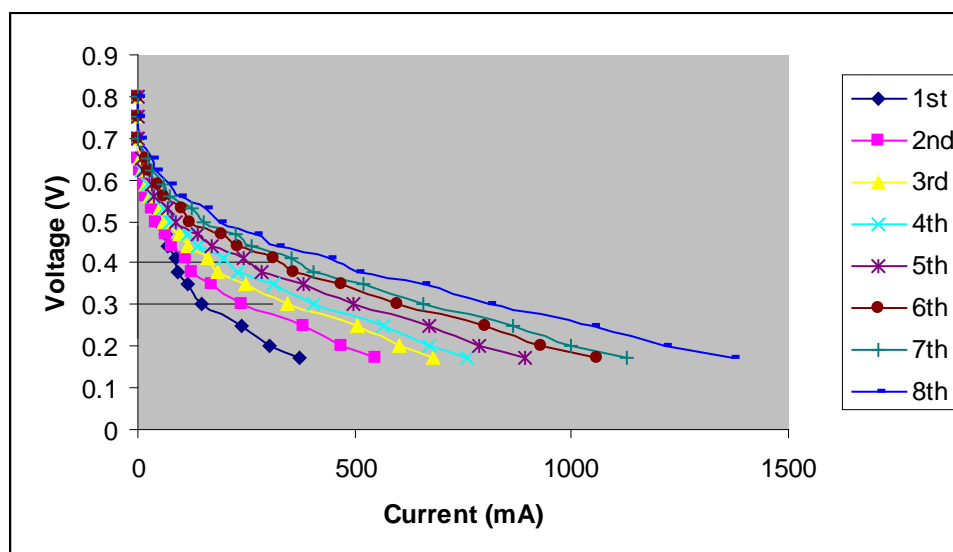
Window

Paint Method: Paper,

Using Heating Plate



Results of Conditioning: The image below shows the increase in performance of an MEA consisting of an in-house prepared anode and a store bought cathode as it is run for an extended time. The legend designates which test corresponds to each line, where 1st is the original test run, and the 8th test is the 8th run. Each run lasted roughly 20 minutes.



VII. APPENDIX B

Review of Reference xix:

A sodium borohydride reduction method for formulating Pd/C has been documented by the University of Illinois^{xix}. In the paper titled “Unusually active palladium-based catalysts for the electrooxidation of formic acid”^{xix}, the sodium borohydride process is described in detail, and the results of using different Pd-based catalysts are examined. The significance of the paper lies in the procedure for preparing 40wt% Pd/C, and the results obtained from the catalyst, since these results can be compared to those obtained by Wright State University.

The five types of Pd-based catalysts that were considered consisted of two palladium blacks (20m²/g from Alfa Aesar and 50m²/g from Sigma-Aldrich) and three carbon supported palladium catalysts (20wt% Pd/C, 40wt% Pd/C, and 20wt% PdAu/C). Each carbon-supported catalyst was prepared through a sodium borohydride reduction process, but instead of preparing the catalyst in a small quantity (in 100mL solutions), the catalyst was prepared in 1L solutions.

The catalyst inks were prepared by making a solution of Millipore water, 5wt% Nafion solution, and catalyst particles. No information is given about the proportions of the ingredients or a stirring procedure for the catalyst inks. Instead of applying the ink to

the GDL, the ink was applied directly to the membrane. In the case of the 40wt% Pd/C, the catalyst loading on the GDE was 2.4 mg Pd/cm^2 . The cathode catalyst consisted of platinum black nanoparticles with a loading of 8 mg/cm^2 . Both sides of the carbon cloth used in the cathode GDE were Teflon coated to assist water management in the cathode. The MEAs were conditioned inside of a fuel cell under H_2/O_2 at 60C for 2 hours.

When examining TEM images of the 20wt% Pd/C, it was noted that the particle size of the Pd seemed to range from 3-10nm, with a few areas containing Pd forming agglomerations that were up to 30nm. When the 40wt% Pd/C was examined by TEM, there were even greater agglomeration issues (50-70nm).

For the 40wt% Pd/C catalyst, a maximum current of approximately 3.5A was obtained at 0.17V and 30C. In comparison, the FAFC prepared at Wright State University had a current of around 2.1A at 0.17V and 60C. It should be noted that there was a 30C temperature difference between the data being compared. At 30C, the MEA tested at Wright State University could not perform well because less energy is available to increase the kinetic performance of the catalysts.

There are a number of reasons for the better performance of the MEA prepared by the University of Illinois. First of all, the loading of the catalyst on the GDE is much greater for the University of Illinois' MEAs (2.4 mg Pd/cm^2 compared to 1 mg Pd/cm^2 at the anode, and 8 mg Pt/cm^2 compared to 1 mg Pd/cm^2). Secondly, the catalyst ink was applied directly to the membrane by The University of Illinois, but it was applied to the GDL at Wright State University because the proper equipment was not available to paint it onto the membrane. Lastly, a different membrane thickness was used. At Wright State University, the type of membrane that was used was Nafion 117 ($175 \mu\text{m}$ thick). The type

of Nafion used by The University of Illinois was Nafion 112 (50 μ m thick). The combination of the difference in membrane thickness combined with the use of platinum at the cathode by The University of Illinois, would seem to lead to a very significant cross-over issue (the reduced thickness would cause cross-over to be an even more significant issue, while the platinum would cause the cathode to be poisonable).

In conclusion, while the results obtained by The University of Illinois were better, many factors played a part, and a significant question arises. The catalyst loading at the anode and cathode was heavier (much heavier for the cathode). This means that much more catalyst was available. The method of ink application was different for both procedures. Lastly, a significantly thinner membrane was used by The University of Illinois. While this could help to reduce the ohmic losses in the cell, it could also introduce very significant cross-over issues. Since platinum is used at the cathode, these cross-over issues could lead to the cathode being poisoned. It is not apparent how this poisoning issue was avoided (perhaps by coating the cathode GDE with Teflon), but if it can be avoided, then using thinner membrane could help to increase the performance of the cell.

VIII. APPENDIX C

Review of Reference xxii:

While the hybrid DFAFC configuration used by Wright State University was unique, it is of interest to also consider other hybrid DFAFC systems that have been designed. Reference xxii specifically considers a unique hybrid DFAFC system which was designed and used to power a laptop computer.

In order to create a hybrid system that would provide enough power to allow a laptop to function under normal circumstances as well as high power situations (turning the laptop on, opening a program, etc...), it was necessary to include multiple components in the system. The complete hybrid system consisted of a 15 MEA DFAFC stack, a miniature liquid pump, a miniature air compressor, cooling fans, a small battery, and a power conditioning control board.

The miniature liquid pump is used to feed the formic acid into the anode. The initial concentration of the fuel being fed into the cell is 11M. The exhaust from the anode is fed back into the top of the fuel tank, the CO₂ is allowed to flow out of the circuit, while the unused formic acid is fed back into the tank. As the system runs, the concentration of the fuel decreases, and the necessary flow rate will increase.

The miniature air compressor was used to supply air into the cathode of the cell. Unused air flowed out of the cathode into the room. The cooling fans were used to keep

the MEA stack at an acceptable temperature ($<50^{\circ}\text{C}$). This was done because excessive temperatures can damage the MEA.

The battery was used when the laptop was initially turned on. Though the fuel cell could supply enough power to run the laptop, a battery was used to start up the laptop, and to run it until the fuel cell reached steady-state conditions. Once steady-state was reached, the fuel cell generated enough power to run the laptop and charge the battery.

The case that housed all of the components was 1438cm^2 and weighed 1.8kg when the fuel tank was full. The battery that was previously used to power the laptop was 93cm^2 and weighed 0.16kg , so the current hybrid DFAFC is over an order of magnitude larger and heavier than the battery that was previously used.

While much research has been done on DFAFCs, very few hybrid systems have been built and tested. Since reference xxii was able to build a hybrid system and test it, many factors that have been previously overlooked by research groups were examined. These factors include orientation of the fuel cell (since it is used in a laptop, the fuel cell will not remain in the same orientation at all times), dynamic response, and long term MEA stability when used with a laptop (test was performed over a 3 month period).

The results obtained from the testing showed that a hybrid DFAFC system could be a possible replacement for batteries in laptops in the future, but significant hurdles still stand in the way. These hurdles include life of the cell as well as cost. The hybrid DFAFC system that was used was capable of producing 30W at $60\text{mW}/\text{cm}^2$. The MEA stack was capable of providing nearly all of the power necessary for the laptop to function for over 150 minutes before additional fuel needed to be added to the system. The conclusion is that the analysis of the hybrid DFAFC should help in designing a 2nd-

generation hybrid DFAFC with a three-fold increase in system efficiency and operation time.

IX. REFERENCES

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- ⁱ *Live Market Quotes*, accessed 13 June 2009, <<http://www.kitco.com/market/>>
- ⁱⁱ O'Hayre, Ryan and Cha Suk-Won., Fuel Cell Fundamentals. New York: John Wiley & Sons, 2006.
- ⁱⁱⁱ Brust, Greg 2005, *Ionomers*, The University of Southern Mississippi, accessed 26 October 2007, <<http://www.pslc.ws/mactest/ionomer.htm>>
- ^{iv} Payne, John n.d., *NAFION® PERFLUOROSULFONATE IONOMER MEMBRANES*, Mauritz Group, accessed 24 October 2007, <<http://www.psrc.usm.edu/mauritz/nafiction.html>>
- ^v Crofts, Anthony 1996, *Lecture 12: Proton conduction, stoichiometry*, University of Illinois at Urbana-Champaign, accessed 24 October 2007, <<http://www.life.uiuc.edu/crofts/bioph354/lect12.html>>
- ^{vi} Kobayashi, T., Rikukawa, M., Sanui, K., Ogata, N., 1998, 'Proton-conducting polymer derived from poly(ether-etherketone) and poly(4-phenoxybenzoyl-1,4-phenylene)', *Solid State Ionics*, Volume 106, Issue 3, 1 February 1998, accessed 26 October 2007, <<http://www.ingentaconnect.com>>
- ^{vii} Tess, Roy W., Poehlein, Gary W., Applied Polymer Science. Washington D.C.: American Chemical Society, 1985
- ^{viii} Strong, A. Brent, Plastics: Materials and Processing. Prentice Hall, 2005
- ^{ix} Comyn, J., Polymer Permeability. Springer, 1995
- ^x Kumar, Anil, Gupta, Rakesh K., 'Fundamentals of Polymers', *Chemical Engineering Series*, New York: McGraw-Hill, 1998
- ^{xi} Arico, Antonino Salvatore. *Nanostructured materials for advanced energy conversion and storage devices*. Nature Publishing Group, 2005
- ^{xii} Vielstich, Wolf., Fuel Cells. New York: Wiley-Interscience, 1970, pg. 119-134

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- ^{xiii} Gasteiger, Hubert A., Kocha, Shyam S., Sompalli, Bhaskar, Wagner, Frederick T. 2004, *Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs*. General Motors Corporation, accessed 30 June 2008, <<http://www.sciencedirect.com>>
- ^{xiv} Yan, Qiang, Wu, Junxiao 2008, *Modeling of single catalyst particle in cathode of PEM fuel cells*. Elsevier Ltd., accessed 25 June 2008, <<http://www.sciencedirect.com>>
- ^{xv} Service, Robert F. 2007, 'Platinum in Fuel Cells Gets a Helping Hand', *Science*, Vol. 315, no. 5809, p. 172, 12 January 2007, accessed 20 October 2008, <<http://www.sciencemag.org>>
- ^{xvi} Brouwer, Jack. "MEA Manufacturing – How We Make MEAs and Why?!?!", Power Point Presentaion, Edison Materials Technology Center, 2007
- ^{xvii} Charretier, Fanny, Jaouen, Frederic, Ruggeri, Stephane, and Dodelet, Jean-Pol. 2007, *Fe/N/C non-precious catalysts for PEM fuel cells: Influence of the structural parameters of pristine commercial carbon blacks on their activity for oxygen reduction*. INRS, Energie, Matériaux et Télécommunications, accessed on 23 October 2008, <<http://www.sciencedirect.com>>
- ^{xviii} Lefevre, M., and Dodelet, J. P., *O₂ Reduction in PEM Fuel Cells: Activity and Active Site Structural Information for Catalysts Obtained by the Pyrolysis at High Temperature of Fe Precursors*. American Chemistry Society, accessed 23 October 2008, <<http://pubs.acs.org>>
- ^{xix} Larsen, Robert, Ha, Su, Zakzeski, Joseph, Masel, Richard I. 2005, *Unusually active palladium-based catalysts for the electrooxidation of formic acid*. University of Illinois at Urbana-Champaign, accessed 16 January 2007, <<http://www.sciencedirect.com>>
- ^{xx} Zhang, Jian, Yin, Ge-Ping, Wang, Zhen-Bo, Lai, Qin-Zhi, Cai, Ke-Di 2006, *Effects of hot pressing conditions on the performances of MEAs for direct methanol fuel cells*. Harbin Institute of Technology, accessed 19 April 2007, <<http://www.sciencedirect.com>>
- ^{xxi} Qi, Zhigang, Kaufman, Arthur 2002, *Activation of low temperature PEM fuel cells*. H Power Corporation, accessed 20 April 2007, <<http://www.sciencedirect.com>>
- ^{xxii} Miesse, Craig M., Jung, Won Suk, Jeong, Kyoung-Jin, Lee, Jae Kwang, Lee, Jaeyoung, Han, Jonghee, Yoon, Sung Pil, Nam, Suk Woo, Lim, Tae-Hoon, Hong, Seong-Ahn 2006, *Direct formic acid fuel cell portable power system for the operation of a laptop computer*. Korea Institute of Science and Technology, accessed 27 September 2009, <<http://www.sciencedirect.com>>